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Contents of Volume

Number 1

Academician Nikolai Markovich EMANUEL' 1
D Ya Toptygin

Electrochemical Optical Spectroscopy of Metals 3
A M Brodskii, L I Daikhin, M I Urbakh

Chain Processes and the Non-stationary Nature of the State of the Surface 21
V V Azatyan

Radical Processes in the Adsorption of Olefins on Zeolites 39
A A Slinkin, A V Kucherov

The Structure and Valence Isomerisation of Antiaromatic Compounds 54
M N Glukhovtsev, B Ya Simkin, V I Minkin

New Chemical Agents for Protection against Ionising Radiation 76
V G Yashunskii, V Yu Kovtun

Phosphorohalidites and Phosphoropseudohalidites in the Arbuzov Reaction with Halogen-containing Compounds 98
V A Shokol, B N Kozhushko

Number 2

The Mechanism of the Reaction of Hydrogen with the Metals of the Iron Sub-group 105
L V Babenkova, N M Popova, I N Blagoveshchenskaya

Complexes of Molecular Oxygen with Organic Molecules 117
A L Buchachenko

The Orientation of Nematic Liquid Crystals 129
E S Luk'yanchenko, V A Kozunov, V I Grigos

Conducting Compounds Based on Phthalocyanine Derivatives 144
V B Zhukhovitskii, M L Khidekel', K M Dyumaev

The Application of Cyclopalladated Compounds in Synthesis 153
A D Ryabov

Metal Complex Catalysts for the Hydrogenation of Aromatic and Heterocyclic Compounds 171
E A Karakhanov, A G Dedov, A S Loktev

Intermediate Compounds and Intermediate Reactions in the Synthesis of Oligonucleotides 185
V F Zarytova, D G Knorre

Functional Microanalysis by Chromato-spectrometric Methods 199
Ya L Kostyukovskii, D B Melamed

Number 3

Catalysis by Metalloporphyrins of Reactions Involving Oxidation by Molecular Oxygen and Oxygen-containing Compounds 215
N S Enikolopyan, K A Bogdanova, L V Karmilova, K A Askarov

New Spectroscopic Methods in Gas-Phase Chemical Kinetics 231
O M Sarkisov, S G Cheskis

Phospha-alkynes — Compounds of Monocoordinate Phosphorus 243
E A Ishmaeva, I I Patsanovskii

Substituted Ureas. Methods of Synthesis and Applications 249
T P Vishnyakova, I A Golubeva, E V Glebova

Furo-, Thieno-, and Pyrrolo-[2,3-*d*]pyrimidines 262
R G Melik-Ogandzhanyan, V E Khachatryan, A S Gapoyan

Metal Carbonyl Complexes with Ligands of Biological Origin 277
A A Ioganson

The Macrokinetics and Rheokinetics of the Hardening of Oligomers 293
A Ya Malkin

Number 4

Three-membered Metallocycles 305
S P Gubin

The Structure of Cluster Compounds of Transition Metals and the Limits of Applicability of the Electron Counting Rules for Polyhedral Molecules 323
Yu L Slovokhotov, Yu T Struchkov

The Electronic Structure of Transition Metal Cluster Complexes with Weak- and Strong-field Ligands 344
G P Kostikova, D V Korol'kov

Estimation of the Stability of Clusters with the Aid of the Theory of the Electron Density Functional 361
Yu A Borisov

The Chemistry of the Cluster Compounds of Technetium 373
V I Spitsyn, A F Kuzina, A A Oblova, S V Kryuchkov

Phosphinepalladium and Phosphineplatinum Carbonyl Cluster Compounds 394
N K Eremenko, E G Mednikov, S S Kurasov

Cluster Transition Metal Chalcogenide Halides 408
V E Fedorov, A V Mishchenko, V P Fedin

Number 5

Nikolai Konstantinovich Kochetkov 425
P M Valetskii

Tetrafluoroammonium Salts 426
I V Nikitin, V Ya Rosolovskii

The Possibilities of the Mass-spectrometric Analysis of Involatile and Thermally Unstable Bio-organic Compounds 437
L N Gall', M Ya Turkina

Kinetics of the Oxidation of Mixtures of Organic Substances in the Liquid Phase 452
R V Kucher, I A Opeida

The Modelling of Biological Catalysts 466
A P Purmal', L A Nikolaev

Thiadecalins and Condensed Thiacyclohexanes of the 2-Thiabicyclo[4.3.0]nonane Series 476
S K Klimenko, T V Stolbova

Chemical Reactions of β-Aminoketones 495
G A Gevorgyan, A G Agababyan, O L Mndzhoyan

Number 6

Metallocarbaboranes. Structural Studies in Recent Years 515
A I Yanovskii

Advances in the Study of the Mechanism of the Gas-phase Oxidation of Aldehydes 532
I A Vardanyan, A B Nalbandyan

The Reactions of Acetals with Ozone 544
D L Rakhmankulov, E M Kuramshin, S S Zlotskii

Thioalkylation Reactions 554
V I Dronov, Yu E Nikitin

The Solid-phase Polymerisation of Monomers with Conjugated Acetylenic Groups 562
V M Misin, M I Cherkashin

Physical Chemistry of the Polycondensation of Polyfunctional Nucleophilic Compounds with Polycarboxylic Acid Derivatives 594
N V Karyakin, I B Rabinovich, A L Rusanov

Polymerisation of *N*-Vinylpyrroles 609
B A Trofimov, A I Mikhaleva, L V Morozova

Number 7

Reactions in Organic Crystals 619
V E Shklover, T V Timofeeva

Stabilisation of Disperse Systems by Water-soluble Polymers 645
A A Baran

Transition Metal Carbonyls Combined with Hydrogen Donors as Initiators of the Radical Reduction of Trichloromethyl Compounds 662
R Kh Freidlina, R G Gasanov, N A Kuz'mina, E Ts Chukovskaya

Metal-containing Complexes of Lactams, Imidazoles, and Benzimidazoles and Their Biological Activity 676
S S Kukalenko, B A Bovykin, S I Shestakova, A M Omel'chenko

The Synthesis and Luminescence-spectroscopic Properties of Fluorescent Condensation Polymers 690
N N Barashkov

Functional Derivatives of Polyisobutene 710
Yu A Sangalov, Yu B Yasman

Number 8

Grigorii Alekseevich Razuvaev 723
P M Valetskii

Paramagnetic d^1-Complexes of Biscyclopentadienylvanadium 724
G A Razuvaev, G A Abakumov, V K Cherkasov

The Stability of Organometallic Compounds During Their Synthesis and Decomposition 739
G A Domrachev, L N Zakharov, Yu A Shevelev

Thermal Decomposition and Stabilisation of Poly(vinyl Chloride) 755
B B Troitskii, L S Troitskaya

The Deposition of Epitaxial Layers from the Vapour of Organometallic Compounds 770
B V Zhuk

Spectroscopic Study of the Steric Effects in Organic Compounds of Silicon Subgroup Elements 786
A N Egorochkin

Advances in the Chemistry of Organolanthanides 802
M N Bochkarev, G S Kalinina, L N Bochkarev

Number 9

The Chemical Physics of the Ageing and Stabilisation of Elastomers 817
N M Emanuel'

Reactive Derivatives of Nucleic Acids and Their Components as Affinity Reagents 836
D G Knorre, V V Vlasov

The Applications and Prospects for Further Applications of Biocatalysts in Electrochemical Systems 852
A I Yaropolov, I V Berezin

The Reactivity of Polyfunctional Compounds in Radical Reactions 863
E T Denisov

Activation of Molecular Oxygen by Metal Complexes and Its Role in the Mechanism of Liquid Phase Oxidation 875
I P Skibida

Diffusion and Sorption of Aqueous Electrolyte Solutions in Polymers 885
G E Zaikov

Modification of DNA by Alkylating Compounds 898
K E Kruglyakova

The Peroxide Oxidation of Membrane Lipids and Natural Antioxidants 907
E B Burlakova, N G Khrapova

Kinetics of the Radiation-induced and Photochemical Oxidation of Biomacromolecules in Aqueous Solutions 918
I I Sapezhinskii

Number 10

New Aspects of the Application of Nuclear Magnetic Resonance to the Study of Chemical Exchange Processes 931
A V Aganov, V V Klochkov, Yu Yu Samitov

Kinetics of the Formation of Adsorption Layers at a Solution–Air Interface 948
V B Fainerman

The Heterogeneous-catalytic Activation of Nitrogen and Oxygen Molecules 960
G I Panov

The Coupled Reactions of Oxidation by Hydrogen Peroxide 974
T M Nagiev

Advances in the Development of Methods for the Epoxidation of Olefins 986
V G Dryuk

The Chemistry of Organic Compounds Containing the Thiodiimide Group 1006
A V Zibarev, G G Yakobson

Physicochemical Aspects of the Conversion of Proteins into Food Products 1025
V B Tolstoguzov, E E Braudo, V Ya Grinberg, A N Gurov

Number 11

Photochemistry of Aliphatic and Aromatic Amines 1041
Ya N Malkin, V A Kuz'min

The Chemiluminescence of Organometallic Compounds 1058
G A Tolstikov, R G Bulgakov, V P Kazakov

Organic Reagents in Spectrophotometric Analysis 1074
S B Savvin

Advances in the Field of Organoelemental Polymers 1091
V V Korshak, N M Kozyreva

Kinetics and Mechanism of the Catalytic Cyclotrimerisation and Polycyclotrimerisation of Isocyanates 1104
A K Zhitinkina, N A Shibanova, O G Tarakanov

The Reactivity of 1,3,2-Diheterophosphacyclanes Containing a Pentacoordinate Phosphorus Atom 1126
N A Polezhaeva, R A Cherkasov

Number 12

The Electronic Structure and Reactivity of Palladium Compounds 1151
O V Gritsenko, A A Bagatur'yants, I I Moiseev, V B Kazanskii

The Interconversions of Pyrylium Salts, Pyrans, Pyrones, and Their Open-chain Forms 1167
O V Drygina, A D Garnovskii, A V Kazantsev

Fluorine-containing β-Ketoesters 1185
K I Pashkevich, V I Saloutin

Halogenophilic Reactions Involving Derivatives of Four- and Five-coordinate Phosphorus 1201
B V Timokhin

Isothiocyanates of Phosphorus Acids, *N*-Phosphorylated Thiocarbamates and Thioureas 1210
R M Kamalov, M G Zimin, A N Pudovik

The Synthesis and Properties of Silicon-, Germanium-, Tin-, and Lead-containing s-Triazines 1227
A S Gordetsov, Yu I Dergunov

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Electrochemical Optical Spectroscopy of Metals

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Modern methods of interpreting experimental results obtained by electrochemical optical spectroscopy (EOS) of metal surfaces are discussed. An attempt is made to unify the results so far obtained by this method by searching for correlations between experimental data and the special features of the electronic structure of the metal-electrolyte interface. The comparison is made in the framework of the semi-phenomenological theory.
The bibliography contains 183 references.

CONTENTS

I. Introduction 3
II. Experimentally measurable quantities and basic formulae 3
III. Microscopic electro-modulation mechanisms 6
IV. Adsorption studies 10
V. Electro-reflection from single crystals 14
VI. I.r. spectroscopy 14
VII. Surface plasmon spectroscopy 15
VIII. Surface-enhanced Raman scattering 16

I. INTRODUCTION

In a new method of studying the physicochemical properties of the interface between an electrode and an electrolyte, the metal surface is monitored *in situ* by analysing the reflectance spectra in the frequency range from the infrared to the near ultraviolet. We shall call this field of work, which is the object of the present review, electrochemical optical spectroscopy (EOS). The method exploits the advantages of combining electrochemical and optical procedures: these include the possibility of continuously monitoring the surface and of controlling its state (including adsorption) under equilibrium conditions. Another important consideration is the high precision of the measurements by the potential modulation technique.[1]

The successful application of EOS in these systems has stimulated the transfer to other systems (with suitable modifications) of optical methods developed for the study of electrode—electrolyte interfaces. These methods offer attractive prospects for *in situ* study and control of heterogeneous catalytic processes in non-polar as well as in polar media.

Historically, one of the earliest optical methods which we could classify as EOS is the study of photo-electrochemical processes: it has already been reviewed extensively,[2-4] and will not be considered further here. Our principal aim will be to analyse methods of interpreting the results obtained in recent developments of the EOS method: ellipsometry, electro-reflectance, phase modulation of the reflected light, surface-enhanced Raman scattering spectroscopy, and surface plasmon spectroscopy. We have tried to give a unified presentation of all the results so far reported and to bring existing reviews up to date.[5-14] The conclusions which can legitimately be inferred from EOS data are examined in terms of specific experimental information.

II. EXPERIMENTALLY MEASURABLE QUANTITIES AND BASIC FORMULAE

Most of the experimental optical methods of studying metal electrode surfaces rely on measurements of the characteristics of the reflected light. In the case of elastic reflection of light from a planar, uniform interface these characteristics are expressed through the two complex quantities r_s and r_p (the amplitudes of the reflection coefficients of the s- and p-polarised light respectively). The following parameters are often measured directly: the light reflection coefficient $R_{s(p)} = |r_{s(p)}|^2$, the phase $\delta_{s(p)} = (1/2i)\ln(r_{s(p)}/r^*_{s(p)})$, and the ellipsometric parameters ψ and Δ, defined by the expressions $\tan\psi = |r_p/r_s|$ and $\Delta = \delta_p - \delta_s$. Here $i = (-1)^{1/2}$, and the symbol * denotes the complex conjugate. The quantities r_s and r_p depend on the frequency of the light ω, on the angle of incidence and on the orientation of the surface relative to the symmetry elements of the lattice of the monocrystalline electrode, and (most important in electrochemical applications) on the potential step E and other parameters which characterise the state of the surface.

Studies of the metal—electrolyte interface can give information on the changes in $r_{s(p)}$ caused by changes in the properties of the surface. The most accurate results are obtained by using an electrochemical modulation procedure in which the potential applied to the interface has a periodic component:

$$E = E_0 + \delta E \sin \Omega t; \qquad (1)$$

and by applying noise separation techniques to the full reflected signal a harmonic of frequency Ω can be extracted. For small amplitudes of the modulation δE the $r_{s(p)}$ values (like other characteristics of the system) can be expressed as

$$r_{s(p)} = R^{1/2}_{0s(p)}\, e^{i\delta_{0s(p)}} + \frac{d r_{s(p)}}{d E}\bigg|_{E=E_0} \delta E \sin(\Omega t + \delta'). \qquad (2)$$

where $\delta_{0s(p)}$ and $R_{0s(p)}$ are the phase and the reflection coefficient for a fixed value of the potential step $E = E_0$. Eqn.(2) is correct if the function $dr_{s(p)}/dE$ does not have a singularity at $E = E_0$. This stipulation may not apply in some special cases,[15] which therefore require a special treatment (see Section III). The phase shift δ' in Eqn.(2) is finite if the potential-induced changes in the processes which affect the optical properties of the system are slow enough (i.e. if their characteristic time is $\sim\Omega^{-1}$) (see below, p.5).

Modulation methods include electro-reflectance (ER),[1] in which the quantity $(1/R_{s(p)})dR_{s(p)}/dE$ is measured, modulation ellipsometry,[16] in which $d\Delta/dE$ and $d\psi/dE$ are measured, and the electro-modulation of the reflected phase (ERP) method,[17-19] in which $d\delta_{s,p}/dE$ is measured. The ERP method was first applied successfully very recently.[19]

We can distinguish two stages in the interpretation of light reflection data from an electrode surface and in extracting information on the structure of the electrode/electrolyte interface. The first stage consists in establishing a correlation between the optical characteristics of the surface and experimentally observable quantities. In electrochemical systems the contribution of the surface to the optical response is determined by the properties of different parts of the interface region. The most informative (as regards determining the electronic properties of the metal/electrolyte interface) is the contribution from a region of microscopic thickness (~1 Å) near the electrode surface, in which the electron density varies from values characteristic of the metal to values characteristic of the electrolyte. Another contribution to the optical response comes from the dependence of the dielectric constant of the electrolyte on the potential step in the macroscopic diffusion region near the electrode.

It has been shown[20-28] that the following three complex functions of frequency and potential are the main optical characteristics of the microscopic region:

$$\Delta\varepsilon_{2(3)}(\omega, E) = \int dx_1\, dx_1' \delta\varepsilon_{2(3)}(x_1, x_1'; \omega, E)$$

$$\Delta\varepsilon^{-1}_{(1)}(\omega, E) = \int dx_1\, dx_1' [\varepsilon^{-1}_{(1)}(x_1, x_1'; \omega, E) - \varepsilon_0^{-1}(x_1, \omega)\delta(x_1 - x_1')] \quad (3)$$

where

$$\varepsilon_0(x_1, \omega) = \varepsilon_m(\omega)\theta(-x_1) + \varepsilon_{el}\theta(x_1);$$
$$\delta\varepsilon_{2(3)} = \varepsilon_{2(3)}(x_1, x_1', \omega, E) - \varepsilon_0(x_1, \omega)\delta(x_1 - x_1').$$

Here the X_1 axis is normal to the electrode surface, which coincides with the $x_1 = 0$ plane; $\varepsilon_i(x_1, x_1'; \omega, E)$ are the diagonal components of the dielectric permeability tensor averaged over the surface† (i = 1. 2. 3 for the X_1, X_2, X_3 axes respectively), which describes the linear response of the system to an external electromagnetic field; $\varepsilon_m(\omega) = \varepsilon'_m(\omega) + i\varepsilon''_m(\omega)$ is the bulk dielectric constant of the metal; ε_{el} is the bulk dielectric constant of the electrolyte, which is a real quantity at optical frequencies; $\Theta(x)$ is a function of the step [$\Theta(x) = 1$ for $x > 0$ and $\Theta(x) = 0$ for $x < 0$]. The quantity $\varepsilon^{-1}_{(1)}(x_1, x_1'; \omega, E)$ which appears in Eqn.(3) is defined by the expression

$$\int dx_1'' \varepsilon_1(x_1 x_1''; \omega, E)\, \varepsilon^{-1}_{(1)}(x_1'', x_1'; \omega, E) = \delta(x_1 - x_1'). \quad (4)$$

The metal is assumed to be in the half-space $x_1 < 0$, and the electrolyte in the half-space $x_1 > 0$ (Fig.1). The integration with respect to x_1 is carried out over the whole space. The changes in amplitude of the light reflection coefficients $\Delta r_{s,p} = r_{s,p} - r^F_{s,p}$ are expressed in terms of the quantities (3) as follows:#

$$\frac{\Delta r_s(k_\parallel, \omega)}{r^F_s} = i\frac{2[(\omega^2/c^2)\varepsilon_{el} - k_\parallel^2]^{1/2}}{\varepsilon_{el} - \varepsilon_m}\Delta e_3$$

$$\frac{\Delta r_p(k_\parallel, \omega)}{r^F_p} = -i\frac{2\varepsilon_{el}[(\omega^2/c^2)\varepsilon_{el} - k_\parallel^2]^{1/2}\{[(\omega^2/c^2)\varepsilon_m - k_\parallel^2]\Delta\varepsilon_2 + \varepsilon_m^2 k_\parallel^2 \Delta\varepsilon^{-1}_{(1)}\}}{(\varepsilon_{el} - \varepsilon_m)[(\varepsilon_{el} + \varepsilon_m)k_\parallel^2 - (\omega^2/c^2)\varepsilon_m\varepsilon_{el}]}. \quad (5)$$

Here $r^F_{s,p}$ are the unperturbed reflection amplitudes, determined by the classical Fresnel formulae, and $k_\parallel$ is the projection of the wave vector on the plane of the electrode surface§; the (X_1, X_2) plane is assumed to coincide with the plane of incidence of the light.

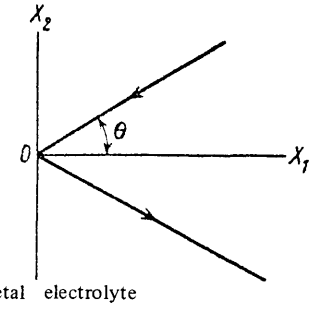

Figure 1. Reflection of light from the metal/electrolyte interface: (X_1, X_2) is the incidence plane of the light, the axis X_3 is normal to the plane of the paper, θ is the angle of incidence.

By using Eqn.(5) for the amplitude $\Delta r_{s,p}$ all the experimentally measured quantities listed above can easily be calculated:

† Throughout this paper the term averaging over the surface will be applied to the process of averaging over a plane parallel to the surface of the electrode and at a distance x_1 from it.

The spatial dispersion of the dielectric constant in the bulk of the metal, which is important only in the silver/electrolyte system at the frequencies used in electrochemistry, is ignored in formulae (5). Formulae which allow for spatial dispersion are given in Refs.20, 21, and 29.

§ Formulae (5) as written are correct if the electrode material has a cubic symmetry (say), and the orientation of the crystal relative to the incidence plane of the light is such that the directions X_1 and X_2 coincide with the crystallographic axes of the crystal. Under these conditions the dielectric permeability tensor $\delta\varepsilon_{ij}(x_1, x_1')$ is diagonalised, $\delta\varepsilon_{ij}(x_1, x_1') = \delta_{ij}\delta\varepsilon_i(x_1, x_1')$. If the surface is isotropic we also have $\delta\varepsilon_2 = \delta\varepsilon_3$. The tensor $\delta\varepsilon_{ij}$ has a diagonal form, and $\delta\varepsilon_2 = \delta\varepsilon_3$, in the frequently encountered case of a polycrystalline electrode. Formulae which apply to this case are given in Refs.20, 21, 28.

$$\frac{1}{R_s}\cdot\frac{dR_s}{dE}=-\frac{4\omega(\varepsilon_{el})^{1/2}\cos\theta}{c}\,\mathrm{Im}\left[\frac{d\Delta\varepsilon_s/dE}{\varepsilon_{el}-\varepsilon_m}\right] \quad (6a)$$

$$\frac{1}{R_p}\frac{dR_p}{dE}=-\frac{4\omega(\varepsilon_{el})^{1/2}\cos\theta}{c}\times$$
$$\times\,\mathrm{Im}\left[\frac{(\varepsilon_m-\varepsilon_{el}\sin^2\theta)\,d\Delta\varepsilon_p/dE+\varepsilon_{el}\varepsilon_m^2\sin^2\theta\,d\,\Delta\varepsilon_{(1)}^{-1}/d\,E]}{(\varepsilon_m-\varepsilon_{el})(\varepsilon_{el}\sin^2\theta-\varepsilon_m\cos^2\theta)}\right] \quad (6b)$$

$$\frac{d\delta_s}{dE}=\frac{2\omega(\varepsilon_{el})^{1/2}\cos\theta}{c}\,\mathrm{Re}\left[\frac{d\Delta\varepsilon_s/d\,E}{\varepsilon_{el}-\varepsilon_m}\right] \quad (6c)$$

$$\frac{d\delta_p}{dE}=\frac{2\omega(\varepsilon_{el})^{1/2}\cos\theta}{c}\,\mathrm{Re}\left[\frac{(\varepsilon_m-\varepsilon_{el}\sin^2\theta)\,d\,\Delta\varepsilon_s/d\,E+\varepsilon_{el}\varepsilon_m^2\sin^2\theta d\Delta\varepsilon_{(1)}^{-1}/d\,E}{(\varepsilon_m-\varepsilon_{el})(\varepsilon_{el}\sin^2\theta-\varepsilon_m\cos^2\theta)}\right] \quad (6d)$$

$$\frac{d\psi}{dE}=-\frac{\tan\psi^F}{1+\tan^2\psi^F}\cdot\frac{4\omega(\varepsilon_{el})^{1/2}\cos\theta}{c}\times$$
$$\times\,\mathrm{Im}\,\frac{\varepsilon_{el}\varepsilon_m^2\sin^2\theta d\Delta\varepsilon_{(1)}^{-1}/dE+\varepsilon_{el}\sin^2\theta\frac{d}{dE}(\Delta\varepsilon_2-\Delta\varepsilon_3)+\varepsilon_m\frac{d}{dE}(\Delta\varepsilon_2-\Delta\varepsilon_3\cos^2\theta)}{(\varepsilon_m-\varepsilon_{el})(\varepsilon_{el}\sin^2\theta-\varepsilon_m\cos^2\theta)} \quad (6e)$$

$$\frac{d\Delta}{dE}=-\frac{2\omega(\varepsilon_{el})^{1/2}\cos\theta}{c}\times$$
$$\times\,\mathrm{Re}\,\frac{\varepsilon_{el}\varepsilon_m^2\sin^2\theta\,d\Delta\varepsilon_{(1)}^{-1}/d\,E+\varepsilon_{el}\sin^2\theta\frac{d}{dE}(\Delta\varepsilon_2-\Delta\varepsilon_3)+\varepsilon_m\frac{d}{dE}(\Delta\varepsilon_2-\Delta\varepsilon_3\cos^2\theta)}{(\varepsilon_m-\varepsilon_{el})(\varepsilon_{el}\sin^2\theta-\varepsilon_m\cos^2\theta)}. \quad (6f)$$

Here $\tan\psi^F=|r_p^F/r_s^F|$. We note that the form of Eqn.(6) is independent of the specific model chosen to describe the optical properties of the surface.

Formulae (6a) and (6b) differ from the expressions obtained from the standard three-layer model,[5] in which two parameters are used to describe the optical properties of a reflecting surface: the thickness d and the dielectric constant ε_l of the transition layer. In the calculation by this model Eqns.(6a) and (6b) are replaced by

$$\frac{1}{R_s}\frac{dR_s}{dE}=-\frac{4d\omega(\varepsilon_{el})^{1/2}\cos\theta}{c}\cdot\frac{d}{dE}\,\mathrm{Im}\,\frac{\varepsilon_l-\varepsilon_m}{\varepsilon_{el}-\varepsilon_m} \quad (7a)$$

$$\frac{1}{R_p}\frac{dR_p}{dE}=\frac{4d\omega(\varepsilon_{el})^{1/2}\cos\theta}{c}\cdot\frac{d}{dE}\cdot\mathrm{Im}\left[\frac{\varepsilon_l-\varepsilon_m}{\varepsilon_m-\varepsilon_{el}}\,\frac{1-\frac{\varepsilon_{el}}{\varepsilon_l\varepsilon_m}(\varepsilon_m+\varepsilon_l)\sin^2\theta}{1-\frac{1}{\varepsilon_m}(\varepsilon_m+\varepsilon_{el})\sin^2\theta}\right] \quad (7b)$$

Whereas the expressions (6a) and (7a) for the reflection of s-polarised light are structurally similar, the expression (6b) for p-polarised light is very different from the corresponding expression (7b) given by the three-layer model. This difference arises partly because in real systems the quantity $\Delta\varepsilon_{(1)}^{-1}$ which appears in (6b) cannot be expressed through the average value of the dielectric constant for the layer (ε_l). However, the most important consideration is that the formal use of the three-layer model (with an anisotropic active layer) complicates the interpretation of experimental data at the microscopic level (see Section III).

Changes in the potential step at the electrode/solution boundary affect not only the electronic properties of the surface but also the distribution of the components in the diffusion layer of the solution, thus affecting the dielectric constant in this region. Hence the measured quantities are determined both by the optical characteristics of the microscopic surface layer and by the characteristics of the macroscopic diffusion layer. In the linear approximation to the interaction of light with the surface region¶ the full ER and ERP signals are described by a sum of terms for the separation effects of these layers. It has been shown[30-32] that under certain conditions the ER and ERP signals are determined by the interaction of the incident light with the macroscopic diffusion layer of the electrolyte. The corresponding expressions for the active components† of the ER and ERP signals are:[32]

$$\left(\frac{1}{R_s}\frac{dR_s}{dE}\right)_a=\sum_i\frac{\partial\varepsilon_{el}}{\partial c_{i,0}}\frac{dc_i(d)}{dE}\cdot\frac{1}{Z_1}\cdot\frac{2l}{(l^4+1)\cos\theta}\times$$
$$\times\{\cos\delta_i[l(1-l^2)-b_1\cos\theta\cdot l^2]+\sin\delta_i\cdot[b_1\cos\theta+l(l^2+1)]\} \quad (8a)$$

$$\left(\frac{d\delta_s}{dE}\right)_a=\frac{1}{2}\sum_i\frac{\partial\varepsilon_{el}}{dc_{i\,0}}\frac{dc_i(d)}{dE}\cdot\frac{l}{(l^4+1)\cos\theta}\times$$
$$\times\left\{\frac{1}{n_{el}^2\cos\theta}[l^2\cos\delta_i-(2+l^4)\sin\delta_i]-\frac{2}{Z_2}[\cos\delta_i(l^2b_2\cos\theta+\right.$$
$$\left.+(1-l^2)l)-\sin\delta_i(b_2\cos\theta-(1+l^2)l)]\right\} \quad (8b)$$

$$\left(\frac{1}{R_p}\frac{dR_p}{dE}\right)_a=\sum_i\frac{\partial\varepsilon_{el}}{\partial c_{i.0}}\frac{dc_i(d)}{dE}\cdot\frac{[4l\cos2\theta]}{l^4+1}\cdot\frac{n_m'n_m''}{f_1(\theta)}\times$$
$$\times\frac{\cos\delta_i[l(1-l^2)-l^2f_1(\theta)]+\sin\delta_i[l(1+l^2)+f_1(\theta)]}{\{[(n_m')^2-(n_m'')^2]\cos^2\theta-n_{el}^2\}^2+4(n_m'n_m'')^2\cos^4\theta} \quad (8c)$$

$$\left(\frac{d\delta_p}{dE}\right)_a=\frac{1}{2}\sum_i\frac{\partial\varepsilon_{el}}{\partial\varepsilon_{i,0}}\cdot\frac{dc_i(d)}{dE}\cdot\frac{l\cos2\theta}{(l^4+1)n_{el}\cos\theta}\left\{\frac{l^2\cos\delta_i-\left(1+\frac{1+l^4}{\cos2\theta}\right)\sin\delta_i}{n_{el}\cos\theta}-\right.$$
$$\left.-\frac{\sqrt{2}\,n_m''\{[(n_m')^2+(n_m'')^2]\cos^2\theta+n_{el}^2\}\{\cos\delta_i[l(1-l^2)+f_2(\theta)l^2]-\sin\delta_i[f_2(\theta)-l(1+l^2)]\}}{[(n_m')^2-(n_m'')^2]^2\cos^2\theta-n_{el}^2]^2+4(n_m'n_m'')^2\cos^4\theta}\right\} \quad (8d)$$

$$l=2\frac{\omega}{c}\xi_0n_{el}\cos\theta;\quad n_{el}=(\varepsilon_{el})^{1/2};$$

$$n_m'+in_m''=(\varepsilon_m)^{1/2};$$

$$b_1=\frac{2\sqrt{2}\,n_m''n_{el}}{(n_m')^2+(n_m'')^2-n_{el}^2};\quad b_2=\frac{\sqrt{2}\,n_{el}[(n_m')^2-(n_m'')^2-n_{el}^2]}{n_m''[(n_m')^2+(n_m'')^2+n_{el}^2]};$$

$$Z_1=\frac{\sqrt{2}\,n_{el}\{[(n_m')^2-(n_m'')^2-n_{el}^2]^2+4(n_m'n_m'')^2\}}{n_m'[(n_m')^2+(n_m'')^2-n_{el}^2]};$$

$$Z_2=\frac{\sqrt{2}\,n_{el}[(n_m')^2-(n_m'')^2-n_{el}^2]^2}{n_m''[(n_m')^2+(n_m'')^2+n_{el}^2]};\quad f_1(\theta)=\frac{2\sqrt{2}\,n_m''n_{el}\cos\theta}{[(n_m')^2+(n_m'')^2]\cos^2\theta-n_{el}^2}$$

$$f_2(\theta)=\frac{\sqrt{2}\,n_{el}\{[(n_m')^2-(n_m'')^2]\cos^2\theta-n_{el}^2\}}{n_m''\{[n_m')^2+(n_m'')^2]\cos^2\theta+n_{el}^2\}}.$$

Here $\xi_0=(2D_i/\Omega)^{1/2}$; D_i and $c_i(d)$ are the diffusion coefficient and the concentration of particles of kind i at the outer boundary of the diffusion layer of thickness d; δ_i is the phase shift between the molecular flow and the potential. In the derivation of these formulae the distribution of concentrations of the various species was expressed by the standard equation[33]

$$c_i(x_1,t)=c_{i,0}+c_i(d)\,e^{-x_1/\xi_0}\sin(\Omega t+\delta_i-x_i/\xi_0-\pi/4), \quad (9)$$

¶ The precision of experimental data does not justify the use of approximations higher than the linear.

† The reactive components $[(1/R_{s(p)}\cdot dR_{s(p)}/dE]_r$ and $(d\delta_{s(p)}/dE)_r$ are obtained from the formulae (8) by replacing the phases δ_i by $\delta_i+(\pi/2)$.

where $c_{i,0}$ is the concentration of particles of kind i in the bulk of the solution. In contrast to Eqn.(6), the quantities in Eqn.(8) show a phase shift with respect to the potential (1). It follows from the formulae (6) and (8) that the angular dependences of $(1/R).(dR/dE)$ and $(d\delta/dE)$, corresponding to the changes in optical properties of the layer of atomic dimensions near the boundary and to the concentration changes in the diffusion layer respectively, are substantially different and can therefore be separated. At low enough frequencies (Ω), when $\xi_0^{-1} > 2\pi c/\omega$, the signal measured at low angles of incidence is determined mainly by the first contribution, and at higher angles of incidence mainly by the second.

III. MICROSCOPIC ELECTRO-MODULATION MECHANISMS

The second main stage in the analysis of light reflectance data is to define the relationship between the parameters $\Delta\varepsilon_{2,3}$ and $\Delta\varepsilon_{(1)}^{-1}$ and the microscopic characteristics of the metal/electrolyte interface, and also to examine the various mechanisms used to modulate the optical properties of the surface. Without these clarifications the information of relevance to chemical studies of the surface phenomena cannot be extracted from the optical data. One possible approach is to use the relationship between the dielectric permeability tensor $\varepsilon_{ij}(\bar{x}, \bar{x}'; \omega)$ and the multi-particle Green function of the system. A simple expression for the non-local dielectric permeability tensor, given by the random phase approximation (RPA),[34,35] is often used at present. This approximation gives a reasonably accurate quantitative relationship between the spectral parameters of the system of electrons in the inhomogeneous medium under study and the behaviour of the reflectance coefficient of the light in the visible and near-u.v. frequency range, without excessively cumbersome formulae.

In the RPA the tensor $\varepsilon_{ij}(\bar{x}, \bar{x}'; \omega)$ is written as

$$\varepsilon_{ij}(\bar{x}, \bar{x}'; \omega) = \varepsilon_p(\bar{x}, \omega)\delta_{ij}\delta(\bar{x} - \bar{x}') + \varepsilon_{ij}^{tr}(\bar{x}, \bar{x}'; \omega) . \qquad (10)$$

The first term in (10) is the plasma component of the dielectric permeability, and the second describes various optical transitions. At the absolute zero of temperature the terms which appear in (10) can be expressed as follows through the Green function:

$$\varepsilon_p(\bar{x}, \omega) = 1 - \frac{4e^2}{m\omega^2}\int d\hat{E}\, 2\Theta(-\hat{E})\,\mathrm{Im}\,G(\bar{x}, \bar{x}'; \hat{E})$$

$$\varepsilon_{ij}^{tr}(\bar{x}, \bar{x}'; \omega) = -\frac{e^2\hbar^2}{m^2\omega^2}\int d\hat{E}\, 2\Theta(-\hat{E})\cdot\left\{\mathrm{Im}\,G(\bar{x}, \bar{x}'; \hat{E})\overleftrightarrow{\frac{\partial}{\partial x_i}}\cdot\right.$$

$$\left.\cdot\overleftrightarrow{\frac{\partial}{\partial x_j'}}G(\bar{x}, \bar{x}'; \hat{E}+\hbar\omega) - \mathrm{Im}\,G(\bar{x}, \bar{x}'; \hat{E})\overleftrightarrow{\frac{\partial}{\partial x_i'}}\overleftrightarrow{\frac{\partial}{\partial x_j}}G^*(\bar{x}, \bar{x}'; \hat{E}-\hbar\omega)\right\}, \qquad (11)$$

where the meaning of the operation $\overleftrightarrow{\partial}/\partial x$ follows from the equality

$$f(\bar{x})\overleftrightarrow{\frac{\partial}{\partial x_i}}g(\bar{x}) = f(\bar{x})\frac{\partial g(\bar{x})}{\partial x_i} - g(\bar{x})\frac{\partial f(\bar{x})}{\partial x_i}$$

Here the symbol $G(\bar{x}, \bar{x}'; \hat{E})$ refers to the one-electron Green function with energy $\hat{E}$, and m and e are the effective mass and the charge of the electron in the metal. Energies are measured from the Fermi level of the metal, and therefore the distribution function at $T = 0$ is of the $2\Theta(-\hat{E})$ type. The integral of the energy which appears in the expression for $\varepsilon_p(\bar{x}, \omega)$ is the distribution of electron density in the system, $\rho(\bar{x})$.

Complete calculations by formulae (11) require extensive information on the electronic structure of the metal/electrolyte system; the procedure is complex and can only be applied in a few special cases, even by using a computer. An alternative approach, less artificial and now widely used, relies on a semi-phenomenological comparison of various properties of the electron spectrum with the behaviour of $\Delta\varepsilon_{2,3}$ and $\Delta\varepsilon_{(1)}^{-1}$ in selected frequency ranges. Approximate expressions for the Green function, which allow a simple physical interpretation, can be used. In the following subsections we shall examine these approximations for different types of spectrum and therefore also for different microscopic mechanisms of the interaction between the light and the surface.

1. Plasma ER

The plasma ER model[36] assumes that the ER effect is due to modulation of the plasma component of the ε_{ij} tensor [first term in (10)] by the change in electron density near the interface caused by the application of the modulation potential, and that the second term in (10) is unaffected by these changes. The latter assumption can be justified only in the range of ω and E values most remote from the photo-emission threshold, and for frequencies far from the optical transition frequencies of the surface layer. The plasma component of the dielectric permeability $\varepsilon_p(x_1, \omega)$, averaged over the surface and allowing also for the collisions between electrons in the bulk of the metal, is often expressed as[10,11]

$$\varepsilon_p(x_1, \omega) = \varepsilon_{el} + (\varepsilon_f(\omega) - \varepsilon_{el})\rho(x_1)/N \qquad (12)$$

$$\varepsilon_f(\omega) = 1 - \frac{\omega_p^2}{\omega(\omega + i/\tau)};\quad \omega_p^2 = 4\pi Ne^2/m;\quad \omega\tau \gg 1 ,$$

where τ is the relaxation time, $\rho(x_1)$ is the electron density (averaged over the surface), and N is the concentration of electrons in the bulk of the metal. For normal incidence of the light on the electrode the model gives the following expression for the relative change in light reflection coefficient and for the phase change:

$$\frac{\Delta R_s}{R_s} = -\frac{4\omega(\varepsilon_{el})^{1/2}}{c}\frac{\Delta Q}{eN}\,\mathrm{Im}\,\frac{\varepsilon_{el} - \varepsilon_f}{\varepsilon_{el} - \varepsilon_m} = -\frac{4\omega(\varepsilon_{el})^{1/2}}{c}\frac{C_{dl}\Delta E}{eN}\,\mathrm{Im}\,\frac{\varepsilon_{el} - \varepsilon_f}{\varepsilon_{el} - \varepsilon_m} \qquad (13a)$$

$$\Delta\delta_s = \frac{2\omega(\varepsilon_{el})^{1/2}\Delta Q}{ceN}\,\mathrm{Re}\,\frac{\varepsilon_{el} - \varepsilon_f}{\varepsilon_{el} - \varepsilon_m} = \frac{2\omega(\varepsilon_{el})^{1/2}C_{dl}\Delta E}{ceN}\,\mathrm{Re}\,\frac{\varepsilon_{el} - \varepsilon_f}{\varepsilon_{el} - \varepsilon_m} \qquad (13b)$$

where

$$\Delta Q = -e\Delta\rho = -e\int dx_1\Delta\rho(x_1);\quad C_{dl} = dQ/dE , \qquad (14)$$

ΔQ is the change in surface charge caused by a change ΔE in the surface potential step, and C_{dl} is the differential double layer capacitance.

According to (13) the intensity of the integral ER signal varies linearly with the density of surface charge, and the differential ER signal is proportional to the differential capacity. These predictions have been confirmed qualitatively for several systems.[37-39] In particular, it was found[38,39] that for $\hbar\omega = 1.3$ eV a lead electrode in 0.1 and 0.25 M solutions of NaF at negative potentials (i.e. in the absence of specific adsorption) gives a linear dependence of $\Delta R/R$ on the charge ΔQ. It follows from (13) that for strongly reflecting metals such as Ag, Au, and Cu, for which $\mathrm{Im}\,\varepsilon_m \ll |\mathrm{Re}\,\varepsilon_m|$, the contribution of the plasma mechanism to $d\delta_s/dE$ is much greater than the contribution to $(1/R_s)dR_s/dE$.

Let us consider the plasma ER in p-polarised light. The quantity $\Delta\varepsilon_{(1)}^{-1}$ in the expression for the ER signal in p-polarised light [unlike $\Delta\varepsilon_{2(3)}$] is strongly dependent not only on the surface charge Q but also on the distribution of electron density $\rho(x_1)$ near the surface. Consider first a simple model for $\rho(x_1)$ [40,41] in which

$$\rho(x_1) = \begin{cases} N - \frac{1}{2}(\beta Q/e + N)\,e^{\beta x_1}, & x_1 < 0 \\ \frac{1}{2}(N - \beta Q/e)\,e^{-\beta x_1}, & x_1 > 0 \end{cases} \qquad (15)$$

Here β is an adjustable parameter, defined by the condition of minimum energy of the ground state of the electron gas in an external field.[41] For metals such as Ag, In, etc. (whose bulk properties are accurately described by the plasma part of the expression for the dielectric constant ε_f) we have, for the condition $|\beta Q| < eN$,

$$\frac{d\,\Delta\varepsilon_{(1)}^{-1}}{dE} \approx \frac{\varepsilon_m - \varepsilon_{el}}{\varepsilon_m\,\varepsilon_{el}}\frac{C_{dl}}{eN} + \frac{1}{\beta^2}\frac{d\beta}{dE}\left[\frac{\varepsilon_m + \varepsilon_{el}}{\varepsilon_m\varepsilon_{el}}\ln\left(-\frac{\varepsilon_m + \varepsilon_{el}}{2}\right) - \right.$$
$$\left. - \frac{1}{\varepsilon_m}\ln(-\varepsilon_m) - \frac{1}{\varepsilon_{el}}\ln\varepsilon_{el} + \frac{i\pi}{\varepsilon_{el}}\right] \qquad (16)$$

This expression shows that the main contribution to $\mathrm{Im}\,(d\,\Delta\varepsilon_{(1)}^{-1}/dE)$ in the case of weak bulk attenuation comes from the region near the point $x_1 = x_1^0$, defined as the solution of the equation $\mathrm{Re}\,\varepsilon_p(x_1) = 0$. This point exists near the surface if the frequency is consistent with $\mathrm{Re}\,\varepsilon_m < 0$, since ε_{el} is always positive. In the frequency range considered the condition $\mathrm{Re}\,\varepsilon_m < 0$ is obeyed by the great majority of metals. When $\mathrm{Re}\,\varepsilon_p(x_1^0)$ vanishes, a positive term proportional to $d\beta/dE$ appears in $(1/R_p)(dR_p/dE)$: this term does not disappear even for the real ε_m values. This effect has been attributed[20,42] to the steep rise of the normal component of the electromagnetic field $\mathscr{E}_1$ at the point $x_1 = x_1^0$, and cannot in principle be described by the three-layer model.

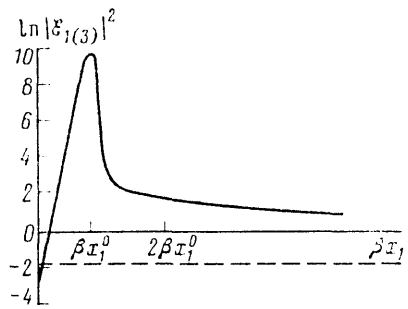

Figure 2. Plots of $\lg|\mathscr{E}_3|^2$ (broken line) and $\ln|\mathscr{E}_1|^2$ (full line) against x_1 for a fixed value of $x_2 = 0$; silver electrode, $\hbar\omega = 2$ eV. The point x_1^0 is found from the condition $\mathrm{Re}\,\varepsilon(x_1^0) = 0$, the parameter β defines the slope of the electron density outside the metal.

The ER spectra in p-polarised light for In and Pb have been calculated[43] by using an expression for $\rho(x_1)$ similar to (15). For $d\beta/dE = 0$ the parameter $(1/R_p)(dR_p/dE)$ for In was found to be negative, becoming positive (in keeping with experimental results[44,45]) for $d\beta^{-1}/dE < -0.02$ Å V^{-1}. For frequencies below the photo-emission threshold (since near the threshold the ER signal is determined by a different effect, see below) the values of $(1/R_p)(dR_p/dE)$ calculated[43] for $d\beta^{-1}/dE = -0.06$ Å V^{-1} agree with the experimental values (see Figs. 3 and 4). It is clear from the experimental results that $d\beta^{-1}/dE$ is very sensitive to the nature of the metal. Thus the study of the plasma ER in p-polarised light can identify the dependence on surface potential of the steepness of the electron density curve outside the metal.

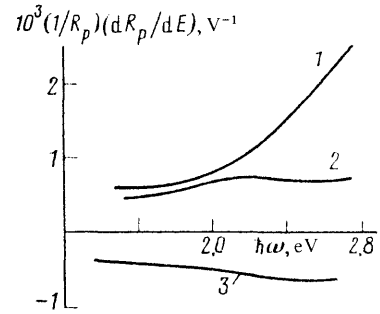

Figure 3. Comparison of the experimental ER spectrum of indium (*1*) in a 0.1 N solution of Na_2SO_4 with theoretical spectra, calculated by the plasma model of ER for $d(1/\beta)/dE$ values of -0.06 Å V^{-1} (curve *2*) and zero (curve *3*), and $E = -1.2$ V (saturated silver chloride electrode);[43] p-polarised light, $\theta = 70°$.

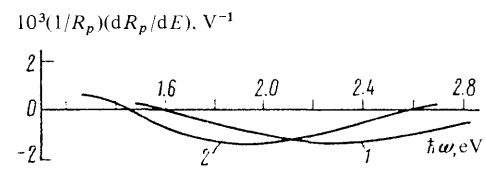

Figure 4. Comparison of the experimental ER spectrum of lead (*1*) in a 0.1 N solution of Na_2SO_4 with the theoretical spectrum (*2*) calculated by the plasma model of ER for $d(1/\beta)/dE = -0.14$ Å V^{-1} and $E = -1.0$ V (saturated silver chloride electrode),[43] p-polarised light, $\theta = 70°$.

Changes in the potential step at the surface can reorient the dipolar solvent molecules near the electrode surface. This effect also leads to a change in the distribution of electron density, and should therefore be observable in electron-reflection in p-polarised light. We have discussed this mechanism[46] using the simplest model of the fixed part of the double layer,[47] i.e. assuming that the solvent dipoles can exist in two states and replacing the discrete distribution of charges from the dipoles by a continuous distribution. The dipole layer is treated as a capacitor in which the density of charge on the plates $q(E)$ is determined by the orientation of the dipoles: $q(E) = ze(N_2 - N_1)/S$, where

N_1 and N_2 are the numbers of dipoles with their positive and their negative pole oriented towards the metal, S is the surface area of the electrode, and ze is the charge on the positive pole of the dipole.[48] The distribution of electron density outside the metal is described by the expression

$$\rho(x_1, E) = \rho_0(E) \exp\left[-2\int_0^{x_1} dx\,((2m/\hbar^2)(W_0 + eU(x, E)))^{1/2}\right], \quad (17)$$

where W_0 is the electronic work function at the zero charge potential (z.c.p.), $U(x, E)$ is the potential distribution in the double layer, and $\rho_0(E)$ is the density of electrons on the electrode surface. By making these assumptions the following expression was obtained[46] for strongly reflecting metals in concentrated electrolytes at potentials close to the z.c.p.:

$$\mathrm{Im}\,\frac{d}{dE}\Delta\varepsilon_{(1)}^{-1} = \frac{\pi^2 e}{\varepsilon_0\varepsilon_{el}(2m/\hbar^2)^{1/2}W_0^{3/2}}\left[C_{dl} + \frac{dq}{dE}\right]x_1^0(0), \quad (18)$$

where

$$x_1^0(0) = \frac{1}{2(2mW_0/\hbar^2)^{1/2}}\ln\frac{(\varepsilon_{el} - \varepsilon_i')\rho_0(0)}{Ne_{el}}, \quad \varepsilon_i' = \mathrm{Re}\,\varepsilon_i.$$

In Eqn.(18) the symbol ε_0 denotes the static dielectric constant of the double layer.

It is clear from (18) that the quantity dq/dE, which defines the rate of reorientation of the dipoles, can be determined in principle by simultaneous treatment of experimental ER and capacitance data. We can show (for example, by model[47] calculations of C_{dl} and q) that in the region of the z.c.p. the reorientation of the dipoles produces a change in sign of the quantity $\mathrm{Im}\,(d\Delta\varepsilon_{(1)}^{-1}/dE)$, and therefore also of $(1/R_p)\cdot(dR_p/dE)$, as compared to a system where reorientation of the adsorbed molecules does not take place. The reason for this effect is that near the double layer, where changes in electric potential have a large effect on the distribution of electron density, the field created by the reorientation of the dipole and the field created by the ions and by the surface charge on the electrode have opposite orientations.

However, not all the effects observed experimentally in the reflection of light by metals can be attributed to modulation of the surface charge. Measurements[49,50] of the electroreflectance and electro-transmittance spectra of s-polarised light for a silver electrode in 1 N Na_2SO_4 solution gave $\mathrm{Re}\Delta\varepsilon$ and $\mathrm{Im}\Delta\varepsilon$ values of similar absolute value but different sign over a wide range of frequency. This result is inconsistent with the prediction from the plasma model that these quantities should have the same sign. The discrepancy was explained[50] by postulating changes in the relaxation time as well as in the concentration of the near-surface electrons in response to changes in the potential step at the surface#. Alternative explanations of the form of the ER signal in s-polarised light at frequencies where the contribution from optical transitions is negligible (and the plasma model should "work") rely on the dependence of the effective mass of the electrons on x_1 near the metal surface. We also note that when conduction is mainly by holes the sign of the ER signal must be the opposite of that given by formula (13a). This may be the reason for the positive sign of the ER signal reported in Ref. 45. Mutually consistent explanations of all these effects would be valuable.

In all the models which allow for the modulation of the surface charge and of the relaxation time the optical characteristics of the surface layer are smooth functions of frequency. Therefore the models cannot explain the experimentally observed maxima and minima in the dependence of $\Delta\varepsilon_{2(3)}$ and $\Delta\varepsilon_{(1)}^{-1}$ on ω. To account for these effects we must allow for the influence of the potential step E on the part of the expression for the dielectric permeability which refers to optical transitions (band-to-band, or within-band, transitions, or transitions involving surface states). The main problem is to identify the physical mechanism of the dependence of $\Delta\varepsilon_{2(3)}$ and $\Delta\varepsilon_{(1)}^{-1}$ on the surface potential step.

2. Effect of Band-to-band and Within-band Optical Transitions

Almost without exception the modulation of band-to-band transitions is described in terms of concepts previously developed to interpret ER in semiconductors. For example, shifts in the Fermi level,[51] bending of the bands,[52] and changes in the relaxation time of band-to-band transitions[53] have been assumed to be produced by the application of an electric field to the sample. That work has already been reviewed in detail.[5,7,9] However, those mechanisms cannot play a major role in metals, because in order to perturb the electronic band structure in the bulk of the metal the external electric field would need to penetrate into the electrode to a depth much greater than atomic dimensions.

A more realistic mechanism of the electro-modulation of band-to-band transitions in metals was suggested in Ref. 54. It applies to the reflection of s-polarised light by polyvalent metals at frequencies close to those of allowed optical transitions between almost parallel bands. It was assumed that at frequencies and potentials far from the photo-emission threshold the dependence of the $\Delta\varepsilon$ tensor on surface potential is determined by the amplitudes of the reflection coefficients of the electron waves incident on the surface from the bulk of the metal. Allowance was made for the dependence on E of the amplitudes of the reflection coefficients of electron waves in the ground and in the excited state. Calculations[54] showed that extrema should appear in the ER spectra at frequencies close to those of allowed band-to-band transitions, due partly to the presence of an interface, which overcomes the requirement of conservation of the normal component of the quasi-momentum in the optical transition, and partly to the possibility of a bulk optical transition in which all the components of the quasi-momentum are conserved. The width of the peak is determined by the mean free path of the electrons in the excited state. A weak dependence of the position of extrema of this type on the surface potential step is typical of bulk optical transitions.

This theory[54] has been used to explain the characteristic features of the ER spectrum of lead in s-polarised light. The band structure of lead[55] contains, near the point W of the Brillouin zone close to the Fermi surface, three almost parallel bands, two of which are partially filled while the third (and uppermost) is empty. Experimental and theoretical frequency dependences of $\hbar\omega\,\mathrm{Im}\,\Delta\varepsilon$ are compared in Fig. 5. The extremum close to $\hbar\omega = 1.2$ eV corresponds to transitions between the highest filled band and the empty band, while the other extremum close to $\hbar\omega = 2.3$ eV corresponds to transitions from the second filled band to the

The possible influence of the modulation of the relaxation time on the ER was first pointed out in Ref. 51. However, allowing for the relaxation time in the dielectric permeability of a thin surface layer poses serious fundamental difficulties.[177]

empty band. Differences between the extrema are ascribed to the special properties of the wave functions of electrons in different bands.

Like the transitions between the electronic bands in the bulk of the metal, transitions involving the surface bands of the metal can affect the dielectric constant of the surface layer. Changes in the surface potential at the metal/electrolyte interface alter the position of the surface band relative to the Fermi level of the metal, thus affecting the contribution from this band to $\Delta\varepsilon_{2(3)}$ and $\Delta\varepsilon^{-1}_{(1)}$. It has been suggested[178] that the maximum at $\hbar\omega = 2.6$ eV observed in the ER spectrum of gold in 1 *N* $HClO_4$ is due to a transition from the surface *d* band to the Fermi level. Increasing the potential shifts the maximum towards lower frequencies, as expected theoretically.[179]

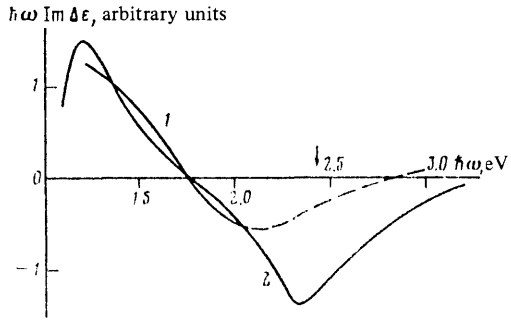

Figure 5. Plots of $\hbar\omega \mathrm{Im}\Delta\varepsilon(\omega)$ against frequency obtained by processing the experimental ER spectrum (*1*) and by calculation (*2*).[54] Lead in a 0.1 M solution of NaF, *s*-polarised light. The broken line is the portion of curve *1* which does not coincide with the calculated relationship because of the photo-emission mechanism of ER; the arrow shows the photo-emission threshold.

The presence of an interface infringes the translational invariance of the system and therefore invalidates the law of conservation of the normal component of the quasi-momentum: optical transitions between states in the same band of the metal therefore become allowed. The contribution of these transitions to the ER should be very sensitive to the structure of the surface: their importance was first pointed out in Ref. 44 and 56. The effect of within-band transitions on the ER signals was later examined in detail,[45, 57–59] using a modulation mechanism based on the effect of the surface potential on the amplitudes of the reflection coefficients of photo-excited electrons at the metal surface. The calculations included the elastic reflection of the electrons from the surface and the possible emission of electrons into the electrolyte.[2] The photo-emission threshold $\hbar\omega_0(E) = \hbar\omega_0 + eE$ (where $\hbar\omega_0$ is the emission threshold at $E = 0$) is a singularity in the electronic spectrum of the metal/electrolyte system. It has been shown[45,57] that this spectral feature is present in the electro-reflectance of the system, and a relationship between the photo-emission current and the ER signal has been obtained.

The existence of a relationship between the photo-emission and the ER offers the possibility of a more rational choice of mechanism for both these phenomena and of extracting more convincing information on the structure of the surface. By combining experimental data on photo-emission and on electro-reflectance we can determine the phases of the matrix elements for the photo-initiated transitions, γ_s and γ_p, which contain information on the surface properties. The phase of γ_p is determined by the properties of the wave functions of the metal electrons in their initial and their final state and by the selection rules of the photo-transition, and depends on the size of the region of the crystal in which the photo-electrons are generated; γ_p is related to the phase of the reflection of the electrons on the Fermi surface from the metal surface.[60] If the photo-excitation is assumed to take place on the surface barrier (surface photo-emission mechanism) the parameter $\tan\gamma_p$ is close to zero.[60] A fairly large value of $\tan\gamma_p$ suggests that the main role in the photo-excitation is played by transitions on the ion cores of the metal near the surface.[61]

For comparison with experiment the most convenient quantities are the second differentials $(1/R)(\mathrm{d}^2R/\mathrm{d}E^2)$ which, like the first differentials $(1/R)(\mathrm{d}R/\mathrm{d}E)$, can be measured directly.[45] The expressions for the second differentials contain fewer parameters, and they identify more precisely the singularity at the threshold. Expressions of the following type have been used[57,60] for $(1/R)(\mathrm{d}^2R/\mathrm{d}E^2)$ in the region of the outer photo-emission threshold:

$$\frac{1}{R}\frac{\mathrm{d}^2R}{\mathrm{d}E^2} = A + B(\hbar\omega - \hbar\omega_0 - eE)^{1/2}\Theta(\hbar\omega - \hbar\omega_0 - eE) + C(\hbar\omega_0 + eE - \hbar\omega)^{1/2}\Theta(\hbar\omega_0 + eE - \hbar\omega). \quad (19)$$

Formula (19) is valid in the vicinity of the photo-emission theshold to with $[(\hbar\omega - \hbar\omega_0 - eE)/\hbar\omega_0]^2$. The parameters *A*, *B*, and *C* in (19) are functions of the frequency and of the angle of incidence: they are independent of *E* and can be expressed in terms of the bulk dielectric constants of the metal and of the electrolyte. The functions are given in an explicit form in Ref. 57.

We should stress that the appearance of the threshold singularity in the expression for $(1/R)(\mathrm{d}^2R/\mathrm{d}E^2)$ is qualitative and unrelated to the details of the calculation. Experimental detection of this singularity is convincing proof of the validity of the chosen physical mechanism of ER.

Formula (19) was obtained by assuming an infinitesimally small amplitude of the modulation δE. However, in experiments the quantity δE is finite, and cannot be too small. Therefore, in view of the singularity in the function $(1/R)\cdot(\mathrm{d}^2R/\mathrm{d}E^2)$, we need to allow more carefully for the non-zero value of δE. An analysis of this problem[15] has shown that a finite value of δE broadens the threshold peaks. In addition to this broadening, however, the fluctuations in the polarisation of the medium near the surface can also affect the dependence of $(1/R)(\mathrm{d}^2R/\mathrm{d}E^2)$ on *E* in the region of the photo-emission threshold. The prospect of characterising these fluctuations is very important in the study of electrode reactions. In order to separate the effect of the polarisation fluctuations we must either design experiments with a smaller modulation amplitude or study systems in which these fluctuations are large.

An analysis of published results[44] shows that the ER of indium, cadmium, lead, and tin includes a substantial contribution from the modulation mechanism considered here. In Fig. 6 the theoretical $(1/R_p)(\mathrm{d}^2R_p/\mathrm{d}E^2)$ curves are compared with experimental curves for indium in a 0.01 *N* solution of Na_2SO_4. In the calculation of the theoretical curves the moduli of the matrix elements were taken from independent photo-emission experiments.[62,63] The phase γ_p of the matrix element of the optical transition excited by a field normal to the surface was treated as an adjustable parameter.

It was found that $\tan\gamma_p = -0.7$, i.e. that the surface mechanism of photo-emission does not play an appreciable part in the case of indium.

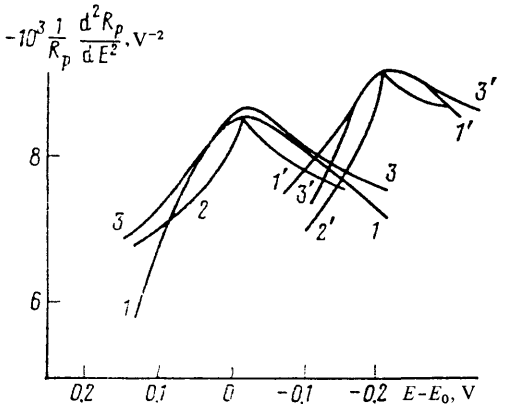

Figure 7. Effect of the modulation amplitude on the potential dependence of $(1/R_p)(d^2R_p/dE^2)$ for indium in a 0.01 *N* solution of Na_2SO_4 with $\theta = 70°$. The experimental curves *1* and *1'* were obtained at frequencies of 2.2 and 2.0 eV respectively, with $\delta E = 0.06$ V.[45] The theoretical curves are for the same frequencies without a correction for broadening (curves *2* and *2'*)[57] and with a correction for broadening (curves *3* and *3'*);[15] $\delta E = 0.06$ V.

Fig. 7, reproduced from Ref. 15, shows the effect of a finite modulation amplitude δE on the threshold behaviour of the ER signal. We note that allowing for instrumental broadening in the theoretical curves brings them into satisfactory agreement with experiment.

IV. ADSORPTION STUDIES

Adsorption on electrodes is one of the basic problems in electrochemistry, and its study is essential to a correct understanding of the mechanism of various electrode reactions. However, the traditional electrochemical methods of determining and studying adsorption, relying exclusively on the measurement of quantities of electricity (i.e. of capacitance), give only limited information. In particular, they cannot distinguish different paths for the transfer of charge between phases. In other words, the quantity of electricity used in the adsorption of the substance is difficult (and sometimes impossible) to separate from the quantity of electricity used in charging the double layer or in the associated Faraday process. The optical methods of studying adsorption discussed in this review usefully complement the traditional methods and offer direct information on the adsorbed species.

1. Determination of Adsorption on an Electrode Surface

Under reversible conditions the adsorption of particles on an electrode surface can be determined strictly by EOS methods.[30-32] Changes in the number of adsorbed particles

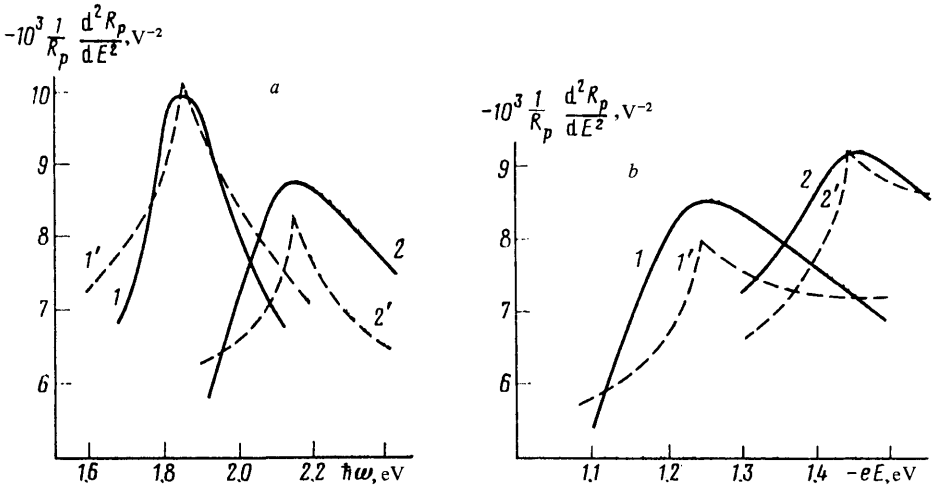

Figure 6. Comparison of experimental and theoretical plots of $(1/R_p)(d^2R_p/dE^2)$ against frequency (*a*) and potential (*b*). The full lines are experimental ER data for indium in a 0.01 *N* solution of Na_2SO_4 for $\theta = 70°$;[45] the broken lines are theoretical;[57] (*a*) curves *1* and *1'* correspond to a potential of −1.6 V, curves *2* and *2'* to −1.3 V (saturated silver chloride electrode); (*b*) curves *1* and *1'* correspond to a frequency of 2.2 eV, curves *2* and *2'* to 2.0 eV.

on the electrode produce changes in the number of particles in the diffusion layer, leading to the experimentally observed effect described by formulae (8). We shall illustrate these effects by considering a 1–1 electrolyte in which neutral molecules of an organic compound are dissolved. Changes in surface potential produce changes in the concentration of particles, both as a result of changes in adsorption and of electro-migration, and the electron-neutrality condition must be obeyed in the region of the diffusion layer. It is easy to show[30,31] that the quantities $dc_i(d)/dE$ and

$$\int_d^\infty dx_1[c_i(x_1)-c_{i0}]$$

which appear in Eqn.(8) can be expressed in terms of the adsorption of particles as follows

$$\frac{d}{dE}c_{org}(d)=\frac{1}{\xi_0}\frac{d\Gamma_{org}}{dE};\quad \frac{dc_A(d)}{dE}=\frac{1}{\xi_0}\left(\frac{\partial\Gamma_A}{dE}+\frac{t^+}{i\Omega F\hat{Z}}\right)$$

$$\frac{dc_B(d)}{dE}=\frac{1}{\xi_0}\left(\frac{d\Gamma_B}{dE}-\frac{t^-}{i\Omega F\hat{Z}}\right)$$

$$\frac{d}{dE}\int_d^\infty dx_1[c_{org}(x_1)-c_{org,0}]=\frac{d\Gamma_{org}}{dE}, \qquad (20)$$

where t^+ and t^- are the transport numbers of the cations (A) and of the anions (B) in the electrolyte; $\hat{Z}$ is the total impedance of the electrode; Γ_{org}, Γ_A, and Γ_B are the surface excesses of the organic compound, the cations, and the anions respectively, equal to the corresponding Gibbs adsorptions under equilibrium conditions; F is the Faraday.

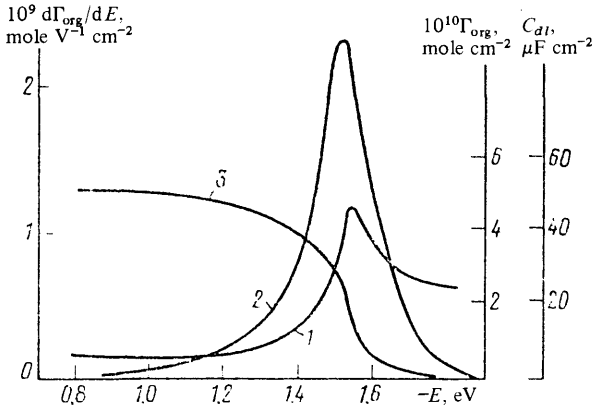

Figure 8. Dependence of the differential capacity (*1*), $d\Gamma_{org}/dE$ (*2*), and Γ_{org} (*3*) on the potential of a lead electrode in a solution of 0.5 *N* Na_2SO_4 + 0.1 M n-C_4H_9OH; modulation frequency Ω = 375 Hz.[30]

By combining formulae (20) and (8b) it has been shown[30] that if the solution is free from organic impurities the differentials $d\Gamma_A/dE$ and $d\Gamma_B/dE$ can be determined as a function of the potential step from the experimental dependence of the impedance $\hat{Z}$ and of $d\delta/dE$ on E. The dependences of $d\Gamma_{A,B}/dE$ on E thus obtained[30] for a lead electrode in a 0.5 *N* solution of Na_2SO_4 are consistent with the result of the Gouy–Chapman theory. If the solution contains an organic substance the above experiments are insufficient to determine $d\Gamma_{org}/dE$, and furthermore the dependence of $d\Gamma_{A,B}/dE$ on E must be calculated theoretically.

The same paper[30] discusses the system consisting of a lead electrode in a 0.5 *N* Na_2SO_4 + 0.1 M n-C_4H_9OH solution. The $d\Gamma_{org}/dE$ curve (curve *2* of Fig.8) was plotted from experimental results by using the dependence of $d\Gamma_{Na^+}/dE$ on E calculated by the Gouy–Chapman theory.

Curve *3* in Fig.8, obtained by integrating curve *2*, is a plot of Γ_{org} against E. The maximum value of Γ_{org} is 5×10^{-10} mole cm^{-2}, which agrees well with the limiting adsorption on mercury.

The contribution of the diffusion layer to ER was first detected[31] in the system indium electrode in a 0.5 *N* Na_2SO_4 + 0.1 M n-C_4H_9OH solution. The most characteristic feature of this ER mechanism is the dependence of the signal on the modulation frequency of the surface potential [see formula (8)].

We should stress that the method gives direct information on adsorption by solid electrodes without an assumed model. Recent work[30-32] should provide a foundation for the development of adequate experimental techniques for determining adsorption by this method.

The method can be used also to study the kinetics of processes taking place near a surface. In particular, by combining it with the photo-emission method of modulating surface concentrations of particles[64] we can, in principle, study fast processes (up to the picosecond range).

2. Determination of the Microscopic Characteristics of Adsorbed Particles

The most important property of optical modulation methods is their ability to provide direct information on the electronic structure of adsorbed particles, on their vibrations, intermolecular interactions, charge transfer, and other microscopic characteristics. This is exactly the information which was lacking in studies of the electrode/solution interface.

Adsorption produces a large change in the electron spectrum of the metal/electrolyte system. As a result of their interaction with the metal the electronic levels of the adsorbed species (atoms and molecules) are both shifted (by an amount Λ) and broadened (by an amount Δ). The parameters Λ and Δ are the basic microscopic characteristics of the adsorbed particles. They depend on the electronic structure of the isolated particles, on the band structure of the metal, and on the potential step at the interface. A knowledge of Λ and Δ is essential for the solution of many problems in the thermodynamics and kinetics of surface phenomena. In particular, the charge q_a on the adsorbed particle[65] can be expressed through Λ and Δ:

$$q_a=Z_a+\frac{2}{\pi}\left[\arctan\frac{\hat{E}_0+\Lambda}{\Delta}-\frac{\pi}{2}\right], \qquad (21)$$

where Z_a is the charge on the ion core of the adsorbed particle, and $\hat{E}_0$ is the position of the energy level of the isolated particle relative to the Fermi level of the metal.

The appearance of new energy levels creates new paths for the adsorption of light, based on electronic transitions from the filled levels of the adsorbed particle to the conduction band of the metal or to the external medium, from the metal to the empty levels of the adsorbed particle, and between the levels of the adsorbed particle. The corresponding changes in the optical properties of the system can in principle be determined by spectroscopic modulation methods.

In order to extract the relevant information from spectroscopic data we need to know the relation between the functions $\Delta\varepsilon_{2(3)}$ and $\Delta\varepsilon^{-1}_{(1)}$ which appear in Eqn.(6) for the experimentally measurable quantities, and also between the parameters Λ and Δ.

Let us consider first the case of small interactions between the adsorbed particles, so that $\Delta\varepsilon_{2(3)}$ can be assumed to be proportional to the number of adsorbed particles N_a. For an adatom with one s level lying below the Fermi level of the metal the imaginary part of $\Delta\varepsilon_{2(3)}$ can be expressed as[66,67]

$$\Delta\varepsilon''_{2(3)}(\omega, E) \sim \frac{N_a}{\omega^4}\rho(0)\left[\arctan\frac{\hat{E}_0+\Lambda+\hbar\omega}{\Delta} - \arctan\frac{\hat{E}_0+\Lambda}{\Delta}\right], \quad (22)$$

where $\rho(0)$ is the density of states having unit orbital momentum on the Fermi surface. In this case the quantity $\Delta\varepsilon''_{2(3)}$ refers to an optical transition from a filled (or partially filled) level of the adatom to the conduction band of the metal. The real part $\Delta\varepsilon'_{2(3)}$ is expressed in terms of $\Delta\varepsilon''_{2(3)}$ by using the Kramers–Kronig relation.

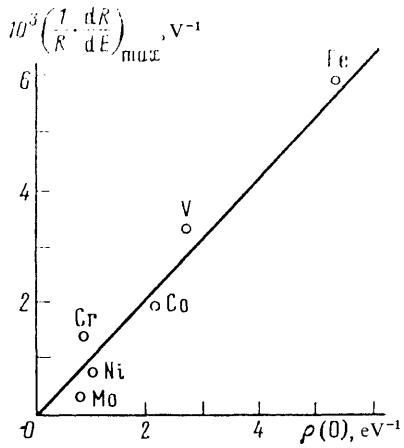

Figure 9. Dependence of the maximum in the ER signal $[(1/R)(dR/dE)]_{max}$ on the density of electronic states at the Fermi level of the metal $\rho(0)$ (calculated per metal atom).[68]

Similar formulae have been obtained[66,67] for transitions from filled states of the metal to empty levels of the adatoms. It follows from (22) that the function $\Delta\varepsilon''_{2(3)}$ has a maximum in the region of the frequency $\hbar\omega_{max} = |\hat{E}_0 + \Lambda|$, and is asymmetric with respect to this frequency. The physical meaning of the formula (22) is relatively simple: the imaginary part of the dielectric permeability tensor is proportional to the product of the number of filled initial states (the term in square brackets) and the number of final states ρ_0 into which the transition can take place. Since $\Delta\varepsilon'_{2(3)}$ is related to $\Delta\varepsilon''_{2(3)}$ by the Kramers–Kronig transformation we can easily show that at $\omega \cong \omega_{max}$ we have $|\Delta\varepsilon'_{2(3)}(\omega)| \ll |\Delta\varepsilon''_{2(3)}(\omega)|$. Therefore it follows from (6a) and (22) that $\Delta R_S/R_S$ goes through a maximum at $\omega \cong \omega_{max}$, so that in the adsorption of the same atoms on different metals $(\Delta R_S/R_S)_{max}$ is proportional to $\rho(0)$. This behaviour of $(\Delta R_S/R_S)_{max}$ has been observed experimentally[68] in a study of the adsorption of water on various transition metals (see Fig.9).

This theory has been applied[69] to the results of experiments on the adsorption of atomic oxygen on platinum immersed in a solution of 0.01 N H_2SO_4 + 1 N Na_2SO_4 at a potential of E = 900 mV relative to the normal hydrogen electrode. The results[69] clearly show a characteristic maximum in the ER signal at frequencies in the range 1.5 eV < $\hbar\omega$ < 3 eV. By comparing these curves[69] with the formulae of Refs.66 and 67 we conclude that in the adsorption of oxygen on platinum (at 0.5 monolayer coverage) the highest initially unoccupied 2p level of the oxygen atom is converted into a resonance level lying 2 eV below the Fermi level of platinum and having a width Δ = 0.3 eV.

At the light frequencies used in ER experiments ($\hbar\omega \cong$ 1.5 to 4.5 eV) electronic transitions to the outer medium are possible for adatom levels lying close to the Fermi surface. We have known[70] that $d\Delta\varepsilon''/dE$ can vary quite sharply near the frequency $\hbar\omega \cong \hbar\omega_e(E) = -\hat{E}_0 - \Lambda + \hbar\omega + eE$, which is the threshold for the transition of the electron from the adatom level of energy $\hat{E}_0 + \Lambda$ to the outer medium. The form of the ER signal is strongly dependent on the symmetry of the wave function of the highest filled state of the adatom.

The expression (6b) for $(1/R_p)(dR_p/dE)$ includes, as well as $d\Delta\varepsilon_{(2,3)}/dE$, the quantity $d\Delta\varepsilon^{-1}_{(1)}/dE$, which can be expressed as

$$\frac{d}{dE}\Delta\varepsilon^{-1}_{(1)} = -\int dx\,dx'\,dx''\,dx'''\varepsilon^{-1}_{(1)}(x, x')\left[\frac{d}{dE}\varepsilon_1(x', x'')\right]\varepsilon^{-1}_{(1)}(x'', x'''). \quad (23)$$

Calculations by this formula are cumbersome in general. However, a useful estimate of $d\Delta\varepsilon^{-1}_{(1)}/dE$ can be obtained by the formula

$$\frac{d}{dE}\Delta\varepsilon^{-1}_{(1)} \simeq -\frac{1}{\varepsilon^2_{eff}}\frac{d\,\Delta\varepsilon_1}{dE}, \quad (24)$$

where ε_{eff} is a parameter independent of E and physically equivalent to the dielectric constant of the medium at the adsorption site of the particle. If the adsorbed particle is sufficiently near the metal the parameter ε_{eff} can be replaced by the dielectric constant of the metal.

The effects so far discussed are associated with optical transitions between the levels of an adsorbed particle and the conduction band of the metal, and are usually observed in ER experiments with s- and p-polarised light, i.e. their polarisation selectivity is not high. This property can be explained by the different symmetries of the electronic states of the metal with energies close to the Fermi level. As a result, whatever the direction of the applied electromagnetic field, we find an allowed optical transition from a level (or to a level) of the adsorbed particle having the prescribed symmetry. However, it has been shown experimentally[71,72] that adsorption can also cause changes in the ER spectra in which the selectivity is marked (the changes in the ER signal caused by adsorption being stronger in p-polarised light than in s-polarised light).

The selectivity of ER is partly due to the bulk optical properties of the metal. The electromagnetic field experienced by the particle is proportional to $1 + r^F_s$ in the case of s-polarised light, and in the case of p-polarised light the normal component of the active field is proportional to $(1 + r^F_p)\sin\theta$. In the optical frequency range for most metals $\varepsilon'_m \ll -1$, and therefore r^F_s is close to -1 and r^F_p is close to 1. Therefore if the angle of incidence is not too small the field acting on the particles is substantially greater for p-polarisation than for s-polarisation of the incident wave. The selectivity of the ER can also be attributed to the increase in the normal component $\mathscr{E}_1$ of

the electromagnetic field near the surface. We note that near the surface the field is $\mathscr{E}_1(x_1) = D_1(0)/\varepsilon(x_1, \omega)$, where $D_1(x_1)$ is the normal component of the electromagnetic induction, which varies only slowly near the surface. Therefore in the neighbourhood of the point $x_1 = x_1^0$, where $\mathrm{Re}\,\varepsilon(x_1^0, \omega) = 0$, the intensity of the field $\mathscr{E}_1(x_1)$ increases (see Fig. 2) if the absorption $\varepsilon''(x_1^0, \omega)$ is small at this point. These effects are not directly related to adsorption, and are typical of any microscopic mechanism of ER and ERP. As a result, signals measured in *p*-polarised light are usually stronger than the corresponding signals in *s*-polarised light.

Adsorption can contribute additional polarisation selectivity, due to the optical transitions between the energy levels of the adsorbed particles. In intramolecular transitions the absorption of light is characteristically related to the orientation of the field relative to the symmetry elements of the molecule. Furthermore, adsorption perturbs the symmetry of the states of the molecule, the changes being most marked in a direction normal to the metal surface. This makes available to the adsorbed particle transitions which are forbidden to the same particles in solution, but these transitions can only take place under the influence of the component of the electric field of the light wave normal to the surface (i.e. for *p*-polarisation). Hence the effect shows a strong polarisation selectivity.

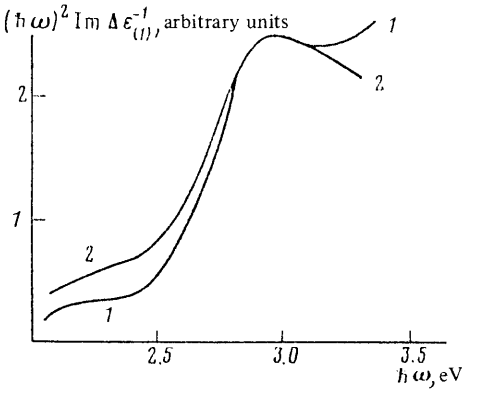

Figure 10. Contribution to the ER of lead from the adsorption of aniline from a solution of 0.1 *N* Na_2SO_4 + 0.0016 M $C_6H_5NH_2$:[73] *1*) experimental plot of the difference between the signals for the above solution and for a solution not containing aniline; *2*) calculated curve.

We have studied[73] the ER of lead in a solution of 0.1 *N* Na_2SO_4 + 1.6×10^{-3} M $C_6H_5NH_2$, allowing for intramolecular optical transitions in the aniline molecules adsorbed on the lead surface. The ER spectra of the lead + aniline system differ from those of pure lead by the appearance of a new minimum in the ER signal at $\hbar\omega = 2.8$ eV in *p*-polarised light, whereas in *s*-polarised light the change in the signal is only slight.[71,72] At this aniline concentration and at a potential $E = -0.7$ V (relative to the silver chloride electrode) the adsorbed aniline molecules are arranged mainly parallel to the lead surface, and furthermore the rate of change in the number of adsorbed molecules oriented normally to the surface is almost zero. This suggests that only adsorbed molecules parallel to the metal surface can affect the ER signal.

Partial charge transfer from the metal to the molecule has been detected electrochemically for the "parallel" adsorption of aniline. Therefore in analysing the experimental results[73] the $^3B_{1u}$ level (which is unoccupied in the molecules in solution) was assumed to be partially filled in adsorption. In this case the observed minimum in the ER signal can be attributed to an optical transition from this level to the $^3B_{2u}$ state. We should stress that this transition is forbidden in the bulk and becomes allowed only under the influence of the normal component of the electric field of the *p*-polarised light, which perturbs the symmetry of the adsorbed molecule in relation to its plane. The symmetry of the initial molecule allows only transitions between these levels in the relevant frequency region.[74]

Theoretical calculations are compared with experimental data in Fig. 10. In the processing of the experiment we found the initial and the final state relative to the Fermi level to be $E_i = 0.4$ eV and $E_f = 2.8$ eV, and their widths to be $\Delta_i = 0.3$ eV and $\Delta_f = 0.4$ eV. From these values of $\hat{E}_{i(f)}$ and $\Delta_{i(f)}$ the charge transfer to the adsorbed molecule can be calculated. By using formula (21) we find $q \approx 0.2$, which is consistent with electrochemical results.

3. Effect of Coverage on the ER Spectra

Experimental results[50,75-83] show that in many cases the ER signal is proportional to the differential with respect to potential of the number of adsorbed particles N_a per unit surface area, dN_a/dE, even at coverages close to a monolayer. For example, in experiments on the dependence of $\Delta R/R$ on the surface coverage of Au and Ag by Pb, Tl, and Cu [82] it was found that in the frequency region where the spectral changes resulting from adsorption do not include structural effects from optical transitions the signal is linearly dependent on N_a at all coverages up to monolayer coverage.

A recent reviewer[84] has explained these results through the effect of the adsorbate on the optical properties of the substrate. One possible mechanism of this effect is a change in the plasma component of the ER due to partial charge transfer between the adsorbed particle and the electrode during adsorption (chemisorption). Electrons injected into the metal influence the density of electrons in the conduction band near the interface and contribute to the plasma component of the ER. In this case the expression for $d\Delta\varepsilon_{2(3)}/dE$ becomes[73]

$$\frac{\mathrm{d}}{\mathrm{d}E}\Delta\varepsilon_{2(3)}(\omega, E) = (\varepsilon_{el} - \varepsilon_f)\left[C_a - \frac{\mathrm{d}}{\mathrm{d}E}(q^{tr}N_a)\right]/eN, \qquad (25)$$

where $C_a(E)$ is the differential capacity of the double layer in the presence of the adsorbed molecules; q^{tr} is the charge of the electrons transferred to the electrode; in the case of charge transfer to the molecule the parameter q^{tr} in Eqn. (25) appears with a minus sign. The ER spectrum produced by this mechanism is similar to the plasma ER spectrum of the pure metal and is determined by the frequency dependence of the dielectric constant of the metal. When q^{tr} is only weakly dependent on N_a the parameter $\Delta R_S/R_S$ is proportional to N_a. It also follows from formula (25) that (in contrast to the plasma ER from a pure surface) in this case the quantity $d\Delta\varepsilon'_{2(3)}/dE$ can be either positive or negative. A change in sign of the plasma component of the ER signal ("inversion" of the plasma ER) has been reported[85] for the adsorption of hydrogen on platinum. Clearly, this observation can be explained by the suggested mechanism.

At frequencies for which the $\Delta R/R$ spectrum is determined by the optical properties of the adsorbate we expect a non-linear dependence of the signal on the coverage of the surface. The effect has been observed in experiments on the adsorption of Cu on Pt and Pb on Pt,[80] and in many other systems.[84]

To explain the experimentally observed non-linearity of the dependence of $\Delta R/R$ on N_a we must allow for the mutual effects between adsorbed particles. In optical experiments these effects may arise mainly for two reasons. On the one hand, because of the effect of adsorbate–adsorbate interactions at higher coverages on the density and other characteristics of the electronic states in the surface layer; the resonance levels of individual adsorbed particles are shifted, their width Γ is changed, and new structures appear, such as a surface band of resonance states.[86] The result is a change in the part of the dielectric permeability tensor (10) corresponding to optical transitions. No detailed discussions of these effects have been published so far: we can only refer to a calculation[87] of $\Delta\varepsilon$ for a metal surface covered with an ordered two-dimensional array of atoms, in which no allowance was made for the interaction with the metal. Starting from the expression for the dielectric permeability tensor (10), (11) in the RPA these workers showed that van Hove singularities in the two-dimensional band structure of the surface layer of atoms can lead to qualitative differences in the reflection coefficients.

On the other hand, at high enough coverages and in the appropriate frequency range the corrections for the local field due to the presence of adsorbed particles may become important. In spite of the many publications already devoted to this topic[83,88–93] the problem is still far from clear. In most of the work so far the surface layer is modelled by a two-dimensional array of dipoles interacting with the light. The results obtained from these models have already been discussed in several reviews.[5,6,83]

A general shortcoming of all the published local field calculations is their reliance on dipole models, which cannot take account of the properties of the adsorbed particles at optical frequencies.[65,94–96] Furthermore, local field effects are important in the same frequency region as the effects caused by changes in the electronic structure of the adsorbed particles as the coverage is increased. This greatly complicates the problems of separating the contributions from different effects. No great reliance can therefore be placed on published comparisons[88–93,97,98] of the local field theory with experiment.

V. ELECTRO-REFLECTION FROM SINGLE CRYSTALS

Until recently ER spectra had been measured mainly on polycrystalline electrodes, with a corresponding loss of information (due to the averaging of the results over all crystallographic directions) and of ease of interpreting the results. Experimental studies of the ER of monocrystals have been reported more recently.[99–109] It was shown that on metals such as Ag, Au, and Cu the ER spectra and their potential dependence depend on the crystallographic face used for the measurement. The effect is not surprising, since the differential capacity, the work function, the matrix elements of the expression for the photo-emission, and the two-dimensional sections of the Brillouin zones are all different on different faces.

Anisotropy of the ER spectra on a clean (110) face of Ag, Cu, and Au crystals was also observed,[99–109] i.e. a dependence of the ER on the orientation of the electric vector of the incident wave with respect to the crystallographic axes of the metal crystal. The anisotropy of the ER is most marked at frequencies close to those of allowed band-to-band transitions.[106] It has been suggested[106] that this effect arises from the anisotropy of bulk band-to-band transitions modulated by the low-frequency field of the double layer.

This phenomenon has been described by using the concepts developed in the theory of ER by semiconductors.[110,111] The double layer field has been assumed[106] to relieve the degeneracy of the bulk states in the region of the critical points lying far from the centre of the Brillouin zone. Under these conditions the matrix elements of the band-to-band transitions become dependent on the angle between the principal symmetry axis at the critical point and the electric vector of the electromagnetic field and of the field of the dipole layer. Furthermore, a model based on the modulation of indirect band-to-band transitions has also been used.[8,99,100] In these studies the azimuthal anisotropy of the ER and the differences in the ER spectra on the (111) and (110) faces of a silver crystal in *s*- and *p*-modulated light were qualitatively accounted for. However, there are serious objections to the application of the suggested mechanism (modulation of the bulk characteristics) to metals.

In contrast to the above approach, based on the anisotropic properties of the bulk states, there have been attempts to relate the azimuthal anisotropy effect to the properties of the surface states of the metal.[109,112] It has been shown theoretically[113] that at the contact between a (110) silver face and an electrolyte a surface band having *s* symmetry is created from the highest level of the bulk band near the Fermi level: this relieves the degeneracy of the *p* states in the bulk band. The bottom of the surface band lies 4 eV above the Fermi level. As a result the matrix element of the transition between states in the bulk band and in the surface *s*-band depends on the direction of the electric component of the electromagnetic field in the plane of the surface: it is zero for $\bar{\mathscr{E}} \parallel \langle 110 \rangle$ and non-zero for $\bar{\mathscr{E}} \perp \langle 110 \rangle$. The quantity dependent on the potential step at the surface is now the bottom of the surface band $\hat{E}_S(E)$. We note that comparison with experiment[109] reveals a strong dependence of $\hat{E}_S$ on E: $(1/e)(dE_S/dE) \cong 3-4$ for the (110) face of a silver crystal. This effect has not been explained satisfactorily so far.

Several papers[80,103,114–117] stress the important role of adsorption factors in the crystallographic and azimuthal anisotropy of ER phenomena. Azimuthal anisotropy in the observed on metal faces which showed no anisotropy in the absence of the adsorbate. A possible explanation is the formation of an anisotropic layer at submonolayer coverages. For example, the adatoms can form regular two-dimensional arrays in which the cell dimensions in two mutually perpendicular directions are very different. At near-monolayer coverages, when the adsorbed lattice is matched to the lattice of the substrate and is therefore isotropic, the ER anisotropy should disappear. This type of dependence of the ER signal on coverage has been observed experimentally.[110] Further theoretical and experimental studies of ER anisotropy are needed to clarify various problems in the structure of adsorbed layers.

VI. I.R. SPECTROSCOPY

Important information on the properties of the metal/electrolyte interface can be obtained by using electrochemical modulation in the i.r. region of the spectrum. By analysing the resulting vibrational spectra we can identify the adsorbed species, determine their mutual arrangement and

their position relative to the atoms of the substrate, and measure their bond lengths and other parameters.[118,119]

However, *in-situ* electrochemical experimentation in the i.r. region of the spectrum is complicated by the absorption of light by the electrolyte under these conditions. As a result, very few attempts to combine i.r. spectroscopy with electrochemistry were reported in recent years, but more recently some significant progress has been made. In a series of investigations[120–123] modulation methods were successfully applied to the study of a platinum electrode in a thin-layer cell. Two different experimental methods were used. In the first the external modulation was supplied through the surface potential step, i.e. this method was essentially the ER technique applied to the i.r. region. The second method, previously used at the metal/vacuum interface, relied on modulation of the polarisation of the incident light. In this case the measured quantity is the difference between the reflection coefficients of *p*- and *s*-polarised light. Unlike the ER method, this technique can be used to determine characteristics of the surface which are not dependent on the potential.

In the i.r. spectra region the vibrational degrees of freedom provide the major contribution to the dielectric permeability tensor. The process obeys the "surface selection rule",[123–125] i.e. the reflection coefficients of the light are unaffected by the vibrations of the adsorbed molecules in directions parallel to the metal surface. The need for this selection rule has been explained as follows. Firstly, as was stated above (p.7), the component of the electric field of the light wave normal to the electrode surface, which acts on the adsorbed molecule, is much greater than the components parallel to the surface (see Fig.2). We should stress that this effect is even more marked in the i.r. than in the visible region. Secondly, it has been suggested[124] that far from the metal surface the fields generated by a dipole parallel to the surface and by its image cancel each other out. However, we note that these conclusions[124] apply only to elastic light scattering, and that very different results may be obtained by allowing for spatial dispersion (screening of the charges), which causes qualitative changes in the pattern of charge distributions.[126] Another possible reason for the enhancement of the effect in *p*-polarised light, mentioned above, has so far been ignored in the publications on i.r. spectroscopy: the increase in the amplitude of the normal component of the field acting on an adsorbed particle resulting from the disappearance of the real part of the dielectric permeability of the system in the vicinity of the surface.

The formulae (6), which are applicable to experiments in the i.r. region, are greatly simplified by the surface selection rule, the terms containing $\Delta\varepsilon_{2(3)}$ effectively vanishing. As a result only the reflection coefficient of the *p*-polarised light is affected by adsorption.

VII. SURFACE PLASMON SPECTROSCOPY

A special type of electromagnetic surface wave (surface polaritons) can exist on solid surfaces: in metals these waves are known as surface plasmons. Surface plasmons are localised near the phase boundary and are propagated along the boundary with a wave vector $\mathbf{k}_\parallel = \mathbf{k}_S(\omega)$, related to the frequency ω by the dispersion law $\omega_S = \omega_S(k_\parallel)$. The dispersion law of surface plasmons is very sensitive to the state of the boundary surface. In electrochemical applications it is important to note that this law depends on the surface potential, on the adsorption, and on the degree of non-uniformity of the surface. The dependence of ω_S on the surface potential was first pointed out in Ref.127. A detailed experimental study of the dependence of $\omega_S(k_\parallel)$ on the potential for silver and gold electrodes in a 0.5 M solution of $NaClO_4$ was later reported.[128,129] Measurements were made both on polycrystalline and on monocrystalline electrodes at potentials believed to exclude specific adsorption. The dependence of ω_S on E was found to change sharply (see Fig.11) near the point of zero charge. For silver at potentials more positive than the point of zero charge the quantity $\hbar\omega_S$ decreases at the rate of $d(\hbar\omega_S)/dE \cong -2 \times 10^{-2}$ eV V^{-1}, whereas at potentials more negative than the point of zero charge $\hbar\omega_S$ is practically constant. Similar experiments in electrolytes containing ions having different polarisabilities gave almost the same results. This means that the effect is produced by the changes in the electronic properties of the metal induced by the changes in the potential step. The effect has been explained[21,130] by postulating a plasma model of the dielectric permeability (12), and the electron density near the point of zero charge was expressed as

$$\rho(x_1) = \rho_0(x_1) - \frac{Q}{e} f(x_1); \int dx_1 f(x_1) = 1, \qquad (26)$$

where $\rho_0(x_1)$ is the distribution of electron density at the point of zero charge ($Q = 0$), and $f(x_1)$ is independent of E.

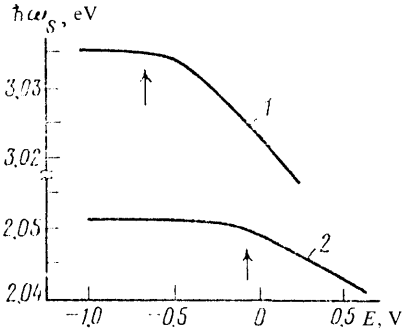

Figure 11. Dependence of the surface plasmon energy on the potential E for polycrystalline Ag (*1*) and Au (*2*) in a 0.5 M solution of $NaClO_4$.[128] E is measured from the potential of the saturated calomel electrode; the arrows denote the points of zero charge.

Explicit forms of the functions $\rho_0(x_1)$ and $f(x_1)$ are given in Ref.131. For the quoted assumptions, the following expression for $d(\hbar\omega_S)/dE$ was obtained:

$$\frac{d(\hbar\omega_s)}{dE} = (\varepsilon_m - \varepsilon_{el}) \frac{C_{dl}(E)}{eN} k_\parallel \hbar B(\omega_s^0) \times \times \left\{1 - \varepsilon_{el}\varepsilon_m \int dx_1 \frac{f(x_1)}{[(\varepsilon_m - \varepsilon_{el})\rho_0(x_1)/N + \varepsilon_{el}]^2}\right\}, \qquad (27)$$

where

$$B(\omega_s^0) = \frac{2(\varepsilon_{el})^{1/2}(-\varepsilon_m)^{3/2}}{(\varepsilon_m - \varepsilon_{el})[\varepsilon_{el}\, d\ln\varepsilon_m/d\omega + 2(\varepsilon_{el} + \varepsilon_m)/\omega]}.$$

Allowing for the steep increase in the differential capacity $C_{dl}(E)$ of this system near the point of zero charge§, Eqn. (27) is qualitatively consistent with experimental results.[128,129]

However, retaining only the first-order terms in Q in the expression for the electron density $\rho(x_1)$ [Eqn.(26)] is justified only at low surface charges (for $Q < 10$ μC cm^{-2}). Therefore Eqn.(27) is valid only in the immediate vicinity of the point of zero charge. To determine the spectrum of surface plasmons over the whole range of potential used in the experiments[128,129] we must allow for the function $f(x_1)$ in (26), and in particular for the dependence of the electron density (β) on E. As was stated above, effects associated with the reorientation of solvent molecules in the double layer may be important in this context. Furthermore, at potentials lying to the right of the point of zero charge oxidation of the electrode is in general possible, and this can substantially affect the $\hbar\omega_s(E)$ dependence. Thus further theoretical and experimental studies are needed to establish unambiguously the electronic structure of the interface between a silver electrode and a solution of an indifferent electrolyte.

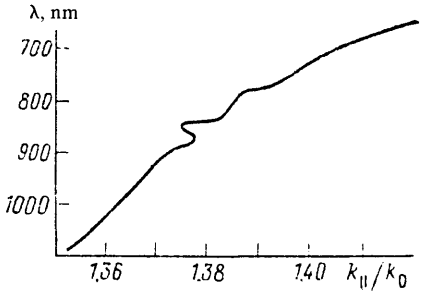

Figure 12. Dispersion curve for the (111) surface of a silver electrode in a 0.1 M solution of NaCl after six activation cycles in the presence of pyridine; $k_0 = \omega/c$.[141]

More than 10 papers have already appeared on the application of surface plasmon spectroscopy to the study of adsorption at metal/air[133–136] and metal/electrolyte interfaces[137–141] (see also the review in Ref.12). The most revealing experiments are the measurements of the frequency dependence of k_s (or of the angle dependence of ω_s) at different potentials. Those measurements were made[141] on a (111) silver face in a solution of 0.1 M NaCl + 10^{-2} M pyridine: they showed that silver–pyridine complexes are formed on the surface, and that they absorb in the region of $\hbar\omega \cong 1.9$ eV. The formation of an absorption region in the surface layer is responsible for some unusual effects in the dispersion curve for the surface plasmons (Fig.12). The double singularity arises from the splitting of the surface plasmon spectrum, which occurs when the resonant frequency for $\Delta\varepsilon_{2(3)}$ or $\Delta\varepsilon_{(1)}^{-1}$ falls into the surface plasmon region. These features in the dispersion curve have been predicted theoretically[142] by using a three-layer model with an absorption region in the surface layer.

Another application of surface plasmon spectroscopy in electrochemical studies should be mentioned. We know from low-energy electron diffraction experiments at the metal/vacuum interface that adsorbates can form superlattices on the surface at sub-monolayer coverages. A similar effect has been observed[143,144] in adsorption at the metal/electrolyte boundary. For example, identical geometrical structures are observed by comparing the adsorptions of Pb on a (111) silver surface in a vacuum and in an electrochemical cell.[145] at low coverages θ_a ($0 < \theta_a < 0.2$) the lead atoms are randomly adsorbed on the surface, but for $0.2 < \theta_a < 0.5$ they form a superstructure of the $(\sqrt{3} \times \sqrt{3})$ type, which disappears at still higher coverages.

The reflection of light from a surface bearing an ordered structure should create surface plasmons with a predetermined value of the wave vector. The effect has been observed[146] in measurements of the differential reflectance ($\Delta R/R$) spectra of a lead-covered (111) silver face. It was shown[146] that at the coverages corresponding to the formation of a superlattice a sharp minimum (denoting the formation of surface plasmons) appears in the $\Delta R/R$ spectrum. The minimum is not observed at low coverages, or at full monolayer coverage. This very important result demonstrates the possibility of obtaining direct information by optical methods on the geometric structure of an adsorbed layer at the metal/electrolyte interface. However, as the authors themselves point out,[146] more experimental results and theoretical studies are needed, and far-reaching conclusions would be premature at present.

VIII. SURFACE-ENHANCED RAMAN SCATTERING

Studies of surface-enhanced Raman scattering occupy a central place in electrochemical optical spectroscopy. The phenomenon, discovered in electrochemical experiments, has stimulated a great deal of interest, both because of its unusual features and through the prospect of new and meaningful ways of studying surfaces. Hundreds of papers, and several reviews, have been written on this topic in the last five years.[162–166,176] The interest shown in this phenomenon is reflected by the original English name ("giant Raman effect") and by the name applied to it in the Soviet literature (anomalously strong Raman scattering, ASRS).

The first report of a Raman scattering (RS) spectrum from pyridine adsorbed on silver was by Fleischmann and coworkers.[147] However, no attempt was made to compare the intensities of the surface and the bulk effect, and the special aspects of the phenomenon were not revealed. Subsequent (though almost simultaneous) publications[148–153] clearly showed that this spectrum is much stronger than the bulk RS spectrum of pyridine. Enhanced Raman effects were soon observed in a large number of systems: aromatic and heterocyclic molecules adsorbed on silver,[148,154] ions adsorbed on silver,[155] and molecules adsorbed on gold and copper electrodes.[156,157] Some very recent papers[158–160] discuss the ASRS from water molecules adsorbed on silver.

The highest enhancement, observed for pyridine adsorbed on a silver electrode, was estimated to be six orders of magnitude. It had been previously assumed that all the adsorbed molecules contribute to the Raman scattering. However, recent work has shown[161] that only a fraction of a monolayer of pyridine is involved in the scattering process. Therefore the enhancement factor could even be 1 or 2 orders

§ A change in Q from −20 to 4 μC cm^{-2} increases the differential capacity from 15 to 130 μF cm^{-2}.[132]

greater. This enhancement effect allows us to study the vibrational characteristics of molecules close to the surface even in the presence of many of the same molecules in the bulk of the electrolyte.

Two explanations have been proposed for the anomalously high intensity of the surface RS. The first relies on the increase in the electromagnetic field near the surface. On an electrode surface, which is rough on a microscopic scale, such an increase can take place through the excitation of surface plasmons.[167,168] This mechanism is controlled mainly by the properties of the metal and of its surface: it is relatively insensitive to the specific characteristics of the adsorbed molecule, and it can therefore be expected to enhance the RS of any molecule which is close enough to the surface. We calculate[169] that the enhancement by this mechanism cannot be greater than two orders of magnitude. A mechanism[171,175] which strengthens the normal component of the electromagnetic field is based on the fact that the real part of the dielectric permittivity of the system vanishes at the point x_1^0 [$\mathrm{Re}\varepsilon(x_1^0, \omega) = 0$]. This mechanism will be effective in RS if the adsorbed molecule is at a distance of approximately x_1^0 from the surface.

The second explanation of the enhanced RS effect depends on the possibility of optical transitions of the electrons from localised surface states (which interact with the vibrations of the adsorbed molecules) into unoccupied states of the conduction band of the metal. It is usually assumed that the localised states are hybridised states of adatoms on the metal electrode and adsorbed molecules.[160,170] Under these conditions resonance Raman scattering (RRS) can take place. However, we should stress that in the case of surface RS the enhancement is due not so much to the fact that the energy of the exciting light is close to the resonance energy (since the state of the adatom–molecule complex is relatively wide) as to the high density of the intermediate states lying near the middle of conduction band of the metal.[171]

Some experimental results can only be explained by the resonance RS hypothesis. For example, on the faces of Ag single crystals no enhancement is observed, and a special pre-treatment of the electrode surface is needed to produce the effect.[170] The treatment consists in alternate formation of a layer of AgCl and reduction to Ag. This produces a large number of Ag adatoms. It has been shown[170,172,173] that the parameters of the absorption band of the adatoms are the same whether they are calculated from the dependence of the ratio of the Stokes and anti-Stokes line intensities on the wavelength of the exciting light or from the ER spectra. This justifies attributing the enhanced RS signal to the presence of adatoms. An irreversible quenching of the enhancement in the Ag + pyridine system has been reported.[174] The effect was produced by applying a cathodic pulse to the surface, causing desorption of the pyridine. At the end of the pulse the RS signal was only 5% of the initial signal, in spite of the readsorption of the pyridine. This observation can be explained by irreversible breakdown of the adatom–adsorbate complexes. Additional evidence in support of the adatom hypothesis is given in Ref.163.

The importance of a knowledge of the angle and polarisation dependence of the Raman scattering cross-section in studies of the mechanism of enhancement has been stressed.[125,171]

Enhanced Raman scattering has already been successfully applied in many laboratories to the study of adsorption. The effect of the surface potential on the orientation of molecules with respect to the electrode surface has been demonstrated by ASRS studies.[152,154] A strong dependence of the shape of the RS line of water on the type of cation and on the pH of the electrolyte has been noted,[160] and it has been suggested[160] that the adsorbed water molecules which contribute to the Raman scattering are not reoriented under the influence of the potential step.

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The results considered in this review convincingly show that EOS methods can provide important information on the microscopic structure of the metal/electrolyte interface and on processes taking place near this interface. EOS methods and their interpretation are now being rapidly developed, and it may be useful to list some of the directions of current work. In methods whose microscopic mechanism is relatively well understood (for example, electro-reflectance) we need many more experimental results, and their interpretation, especially for systems including monocrystalline electrodes. EOS studies of phase transitions in near-surface regions are also of great interest.

The possibilities offered by the spectroscopy of surface plasmons and of other surface excited states (polaritons) have been inadequately exploited so far. It would be interesting, for example, to establish the influence of surface plasmons and polaritons on electrochemical reactions.

The search for a comprehensive explanation of the surface enhancement of Raman scattering by adsorbed molecules is currently of interest. We believe that non-linear processes may play an important role in these phenomena. More data not only on the frequency dependence but also on the polarisation and angular dependence of the intensity of the surface Raman scattering of light are needed to solve these problems.

Second harmonic generation at the boundary between two media and its amplification on rough surfaces are currently of interest.[180–183] This phenomenon is closely related to surface Raman scattering, and is potentially very attractive for studying the microscopic structure of surfaces.

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Chain Processes and the Non-stationary Nature of the State of the Surface

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The reversible non-stationary nature of the solid surface in branched-chain processes (BCP), which is one of the most important factors determining the regular features of chemical reactions of this class, has been demonstrated. The general regular features of non-thermal BCP which have been observed in the last 10-12 years and which are determined by the change in the condition of the surface and in the contribution of heterogeneous processes to the course of chain combustion have been described and systematised. Kinetic models taking account of the non-stationary nature of the surface and the non-unique nature of the stationary states of the system have been discussed.
The bibliography contains 111 references

CONTENTS

I. Introduction 21
II. General characteristics of experimental procedure 22
III. Heterogeneous self-acceleration of branched-chain processes 23
IV. Sorption of the components of the reaction mixture and its role in combustion 26
V. Kinetic models of the heterogeneous self-acceleration of branched-chain processes and a new type of flame propagation 29
VI. Pulsed chain combustion and the non-stationary nature of the state of the surface 33
VII. Heterogeneous self-retardation of branched-chain processes 34

INTRODUCTION

One of the most important and general factors in gas-phase chain processes is the reaction of components of the reaction mixture with solid surfaces. These include the surfaces of the reaction vessel, condensed reaction products, and various solid objects or particles introduced into the reaction medium for different purposes (for example, detectors, powdered quenching agents, etc.). The destruction of active intermediates on a solid surface (heterogeneous destruction). leading to termination of the reaction chains, determines to a large extent the regular features of the chain process, including its kinetics and thermal conditions. Heterogeneous termination also determines the magnitude of the concentration gradients of the chain carriers and the rate of the process as a whole. Heterogeneous termination provides a direct channel for the removal of energy from the reacting gas, and hence to a large extent it also determines the temperature gradients in the reaction medium.

A large number of papers have been devoted to the theoretical and experimental study of chain processes under different conditions of heterogeneous chain termination. By taking account of the destruction of the chain carriers on the surface of the reaction vessel, the theory successfully explains such important characteristic features of branched-chain processes (BCP) as the first self-ignition limit, the dependence of the limit on the dimensions of the reaction vessel and the composition of the mixture, and the dependence of the kinetics of the chain process and the first limit on the material of the walls of the reaction vessel.[1-6] The measurement of the first self-ignition limit provides a basis for methods for determining the rate constants of the homogeneous reactions of chain carriers[7-9] and their heterogeneous destruction (see for example Refs.3, 4, 10, and 11).

In a number of cases, chain initiation, that is the formation of active intermediate products involving only the original valence-saturated molecules, also takes place on the surface.[1,3,12-14] The heterogeneous–homogeneous reactions observed over various catalysts have been attributed to heterogeneous initiation.[12,14]

At the same time, up to the present, there has been very little investigation of the role of the surface in chain reactions. Until recently it was considered that chain termination on the surface was the only heterogeneous stage of the process involving the active intermediates. In the examination of the kinetics of chain processes (both in theory and in the treatment of experimental results), the following original propositions relating to the heterogeneous stages were generally accepted.

1. The adsorption of the chain carriers is identical to the reaction involved in their termination. In the quantitative examination of the kinetics of the process, in the solution of the kinetic equations, including their solution by means of a computer, and also in the treatment of experimental data, it was assumed that the sorbed chain carriers rapidly react with identical species to form the original molecules. The properties of the surface were assumed to remain unchanged during the entire process.

2. The heterogeneous destruction of the chain carriers shows first-order kinetics with respect to the concentration of these particles. Thus in the kinetic equations of the chain processes, heterogeneous termination was described by terms which were linearly dependent on the concentrations of the chain carriers.

3. It was generally assumed that if the first self-ignition limit is stable and the kinetic curves giving the concentrations of the components of the reaction mixture are reproducible, then the coefficient of the heterogeneous destruction of the chain carriers (the probability of their destruction on collision with the surface) is constant throughout the entire process. In the study of gas-phase reactions, the surface of the reaction vessel is "conditioned" beforehand by the reaction being studied, to obtain reproducible results. It was assumed that when reproducibility had been achieved, the state of the surface, the efficiency of the heterogeneous termination, and the coefficient of the destruction of the chain carriers on the surface remained unchanged from the beginning to the end of the chain process. The efficiency of the heterogeneous deactivation of the excited species and the accommodation coefficient for the heterogeneous destruction of the atoms and radicals were also assumed to be constant.

The study of BCP and the heterogeneous reactions of free atoms and radicals, however, led the present author to the conclusion that these original propositions are generally inapplicable.[15,16] In constrast to generally accepted ideas, it was found that during and under the influence of a chain reaction, the properties and functions of the surface may undergo extensive reversible changes, and this may not influence the reproducibility of the results. The changes in the state and role of the surface may be brought about by the following factors, not previously taken into account in the theory of chain processes: the chemical reaction of molecules, atoms, and radicals from the gas phase with the surface; the adsorption non-uniformity of the surface; and the reactions of the adsorbate with components of the gas phase.

The possible development of reaction chains involving sorbed atoms and radicals was also noted.[15,16] For example, the works cited gave the following heterogeneous reactions for the oxidation of hydrogen-containing compounds:

$$H_{sorbed} + O_2 \rightarrow HO_2$$
$$H + HO_2 \rightarrow 2OH$$
$$H + HO_2 \rightarrow H_2O + O$$
$$H + HO_2 \rightarrow H_2 + O_2$$

Some of these reactions lead to the transfer of the chain carriers into the volume. Thus the reaction of O_2 with sorbed H atoms and the subsequent stages can lead to the development of chains, which is equivalent to a decrease in the efficiency of the heterogeneous termination.[15,16]

Since the principal regular features of BCP are determined chiefly by the competition between the processes of chain branching and termination, the above heterogeneous processes and the reversible changes in the properties of the surface should play an important role in the process as a whole. Even when the reaction of a sorbed chain carrier with a gas phase species does not lead to the development of chains, but gives the final product, this increases the rate of the chain process, since it provides an additional channel for the consumption of the starting material. The heterogeneous reactions of atoms and radicals, leading to the development of chains, can obviously take place much more rapidly than the decomposition of the molecules on the surface, accompanied by the removal of radicals into the volume. Because of their high rates, the reactions of the type given in Refs.15 and 16 may play an important role even in the fast processes of developing combustion.

It should be noted that until recently, in the study of BCP, most quantitative measurements under static conditions were related to self-ignition limits and to the kinetics of the reaction above the second limit. At the same time, significant changes in the properties of the surface and a contribution from these changes to the process as a whole are to be expected primarily under combustion conditions, in the course of which high concentrations of active intermediate species are produced. It was in the examination of the experimental data under chain combustion conditions that the present author detected significant deviations from the linear theory (see below).

In Ref.15, in the treatment of experimental data from Ref.17, it was found that the observed rates of combustion of H_2 were several times greater than the values calculated by traditional methods which do not allow for the reversible change in the efficiency of the heterogeneous destruction of the chains during combustion. In Refs.15 and 16 it was also shown that the equations used in Ref.17 and in various other studies for the treatment of the experimental data for the most part do not correspond to the actual process: for most experimental conditions (see for example Ref.17), they lead unambiguously to negative values of the concentrations of the starting materials. This is due to the fact that these equations were obtained by the method of quasi-stationary concentrations, without allowance for the homogeneous nonlinear termination of the chains.

Subsequent experiments showed that the change in the properties and the role of the surface during chain combustion, and the significant influence of these changes on the chain process, are important and general properties of a whole class of branched-chain reactions. The principal results of work in which previously unknown general regular features of branched-chain reactions were detected and studied, and the important role of the reversible nonstationary nature of the properties and functions of the surface in these processes was revealed, are described below.

II. GENERAL CHARACTERISTICS OF EXPERIMENTAL PROCEDURE

In most cases the experiments have been carried out under static conditions using vacuum apparatuses, for the most part the standard assemblies for kinetic experiments. A combined procedure was used, involving the simultaneous recording of various kinetic characteristics of the reaction mixture and the process: the pressure of the mixture, the concentrations of the individual components from absorption spectroscopy, the intensity of the chemiluminescence, and, where necessary, temperature.[18-23] The previously prepared reaction mixture was transferred rapidly from an intermediate volume into an evacuated reaction vessel at the required temperature†. An oscillograph was used to record the above characteristics of the reaction system from the start to the end of the experiment. After the experiment with a given portion of gas, the reaction vessel was evacuated. The extent of the evacuation (to ~10^{-4} mmHg) and the evacuation time (3 min after attaining a pressure of ~10^{-4} mmHg) were kept constant in a given series of measurements.

In addition to the vacuum assemblies with lubricated taps, usually employed for kinetic experiments, a high-vacuum assembly in which the taps with lubricant were replaced by metallic vacuum valve taps (without lubricant) was also used. The evacuation system was separated from the rest of the assembly by these valves and by two traps arranged in series and cooled with liquid nitrogen. In the assembly with metal lubricant-free taps, the gas in both traps came into contact only with the cold walls (so-called traps without a hot wall).[23] In the standard assemblies for kinetic experiments, with lubricated taps, high-vacuum Apiezon N (saturated vapour pressure 10^{-9} mmHg) and sometimes Merck (silicone, 10^{-6} mmHg) lubricants were used. In some series of experiments, the vacuum lubricant produced in the Soviet Union (GOST 380183-75) was also used. The experimental procedure has been described in detail.[18-26] When a process was carried out in the same reaction vessel for identical initial conditions, the results of the measurements were the same, irrespective of the grade of lubricant used. Published data[23] show that the results of the study of BCP in this reaction vessel, even in the kinetic range of chain termination and close to the first ignition limit, are independent of whether the reaction vessel is in an ordinary vacuum assembly with lubricated taps or in an assembly in which metal high-vacuum taps without lubricant are used.

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†In the study of the oxidation of phosphorus vapour, the working mixture was prepared in the reaction vessel.[21]

In most of the studies of this series, the primary aim was to determine whether it is possible to describe chain combustion on the basis of the above generally accepted ideas about the role of the surface, the nature of the heterogeneous reactions of the chain carriers, and the constant efficiency of heterogeneous termination during combustion. In addition to various other kinetic characteristics of BCP, use was also made of one of the most fundamental properties of reactions of this class, namely that chain combustion develops (undergoes self-acceleration) only when the rate of chain branching is greater than the rate of chain termination. For heterogeneous termination, this condition for self-acceleration of the process is determined by the inequality:[1-6]

$$2k_b[B] > k_{het} \quad (1)$$

where k_b is the chain branching rate constant; [B] the concentration of the starting material involved in the branching process; and k_{het} the heterogeneous termination rate "constant".

It can be seen that if the initial concentration of the original molecular substance B is greater than its concentration at the lower limit of self-ignition, for example by 2%, then in the absence of appreciable self-heating of the reaction mixture and positive interaction of the chains, immediately after the combustion of this 2% excess of substance above the limit, the rate of branching will become lower than the rate of termination. As a result, the self-acceleration of the combustion, and then the combustion itself, soon stop. This is the case, however, only if k_{het} is constant during the combustion, as previously assumed. If however in addition to the concentration of the substance B there is also a decrease in the "constant" k_{het}, it is obvious that after the combustion of the excess quantity of the starting material relative to the self-ignition limit, the branching process, for a certain time interval, will remain more rapid than the termination, so that the self-acceleration of the combustion will continue. In this case the self-acceleration of the combustion process will stop only at higher degrees of combustion. Thus if the efficiency of the heterogeneous termination decreases during combustion, the observed degree of combustion at the end of the reaction should be greater than that which would be observed if there were no change in the efficiency of the termination on the surface or in the absence of heterogeneous chain branching.

It can also be seen from Eqn.(1) that if during combustion the value of k_{het}, on the other hand, increases, that is if the efficiency of the termination increases, then the self-acceleration of the chain process will stop before the decreasing concentration of the starting material reaches the value corresponding to the first ignition limit. There is also a decrease in the final degree of combustion.

The final degree of combustion is defined as the fraction of the starting material used up at the end of the combustion:

$$\eta_\infty = \frac{[B]_0 - [B]_\infty}{[B_0]}$$

where $[B]_0$ and $[B]_\infty$ are the concentrations of the starting material at the initial moment and at the end of the combustion respectively.

The first self-ignition limit (P_1) is the average value between two neighbouring initial pressures (P_0), at the lower of which there is no ignition, while at the higher the gas undergoes self-ignition. The ignition was recorded from the chemiluminescence and from the self-accelerating change in the pressure of the mixture, brought about by the change in the number of moles of the gas in the closed volume as a result of the reaction. For the oxidation of silane and phosphorus vapour and the decomposition of NCl_3, the ignition was also recorded from the self-accelerating decrease in the absorption of light of the appropriate wavelength by the starting material. Additional control of the accuracy of the measured ignition limit is made possible by the fact that as the initial pressure approaches the upper limit, the ignition induction period increases sharply, approaching infinity.[19,25]

The degree of combustion can be readily determined from the initial and final pressures and the stoichiometry of the overall process. For example, the equations for the overall processes $2H_2 + O_2 \rightarrow 2H_2O$ and $2CO + O_2 \rightarrow 2CO_2$ show that the decrease in the number of moles of O_2 at the end of the combustion is equal to the decrease in the number of moles of the entire mixture:

$$\Delta[O_2]_\infty = \Delta[M]_\infty \quad (2)$$

where M represents any component of the mixture, and the subscript ∞ refers to the end of the combustion. Thus the degree of transformation of O_2 (degree of combustion) can be determined from the total pressure of the mixture. For a stoichiometric mixture

$$\eta_\infty^{expt} = \frac{(O_2)_0 - (O_2)_\infty}{(O_2)_0} = 3\frac{P_0 - P_\infty}{P_0} \quad (3)$$

The water vapour formed during combustion is absorbed to a large extent by various surfaces.[19,27,28] To determine correctly the final degree of transformation (degree of combustion) in these processes, a procedure has been proposed,[19,25] in which, when combustion has stopped, the water vapour is frozen out, and the residual pressure in the system is then recorded. The experimental value of the degree of combustion is then given by the expression

$$\eta_\infty^{expt} = (P_0 - P_\infty^w)/P_0 \quad (4)$$

where P_∞^w is the pressure after the water vapour has been frozen out.

In the oxidation of silane and phosphorus vapour the decomposition of nitrogen trichloride, the value of η_∞^{expt} was also determined by absorption spectroscopy.[19,20-22,26]

In the region of the first ignition limit and at temperatures appreciably greater than the temperature of the point of the ignition peninsula, heterogeneous termination in fact becomes the only route for the termination of the reaction chains. Moreover, low concentrations of the reagents close to the first ignition limit and relatively long combustion times decrease the self-heating and the role of termolecular reactions in most experiments. In the kinetic range of the chain termination process, however, there is practically no self-heating or termolecular reactions.[19] All this simplifies the interpretation of the results and makes it possible to reach unambiguous conclusions from the experimental data.

III. HETEROGENEOUS SELF-ACCELERATION OF BRANCHED-CHAIN PROCESSES

Fig.1 gives the oscillograms for a series of experiments with detonating gas at different initial pressures in a quartz vessel with a diameter of 5.5 cm, the surface of which was washed with hydrofluoric acid and treated with pulses of the mixture being studied to stabilise the value of the ignition limit and achieve reproducibility of the kinetics of combustion.[19,25] The chemiluminescence oscillograms are not given in Fig.1. The numbering of the curves corresponds to the sequence of the experiments. The quantitative reproducibility is illustrated by the kinetic curves *2* and *6*.

Because of the low pressures and the relatively high temperatures in these experiments, the rate of the heterogeneous disappearance of the H atoms is more than 150 times the rate of the termolecular reaction (VI)#:

$$H+O_2+M\rightarrow HO_2+M \qquad (VI)$$

Thus it is possible, without loss of accuracy, to neglect reaction (VI) and the reactions of those HO_2 radicals which are formed in this termolecular stage. Since the reaction time is much longer than the heat-removal time (by a factor of more than 10^5), there is no self-heating.[19]

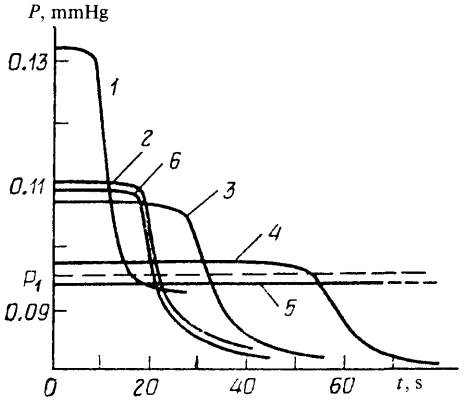

Figure 1. Oscillograms for the change in pressure during the combustion of a $2H_2 + O_2$ mixture at 743 K and different initial pressures (P_1 = 0.095 mmHg).[19,25]

Fig.1 shows that the self-ignition limit P_1 lies between the initial pressures of experiments *4* and *5*, and that, for example, in experiment *4* the magnitude of P_0 and hence the magnitude of $[O_2]_0$ are ~2% greater than the limiting values. If the efficiency of the heterogeneous termination (k_{het}) did not decrease during the combustion, the decrease in pressure accompanying the reaction in experiment *4* would have stopped before the broken line had been reached, that is before P_1. It can be seen from the oscillogram for experiment *4*, however, that the decrease in pressure close to the ignition limit not only does not stop but on the contrary continues to accelerate, even under the limit, reflecting directly the fact that the rate of branching continues to predominate over the rate of chain termination. Since there is no self-heating or purely homogeneous positive interaction of the chains, the predominance of the branching over termination can take place only as a result of a decrease in k_{het} during the combustion. The decrease in the efficiency of the heterogeneous chain termination during the combustion is also indicated by the fact that the combustion stops only after a degree of combustion corresponding to several tens percent O_2, which is greater by an order of magnitude than that expected without allowance for the decrease in the efficiency of the heterogeneous destruction of the chain carriers.

The results of another series of experiments are given in the Table. It can be seen that either ignition does not take place (experiments *3* and *9*), so that there is no combustion, or, if ignition takes place (experiments *1*, *2*, and *4–8*), the reproducible degree of combustion corresponds to tens percent of the mixture, even if the initial concentration is 2% greater than the ignition limit. Thus in this series of experiments at P_0 close to P_1, the degree of combustion is 10 times that expected for a constant efficiency of chain termination.

Final degrees of transformation of a $2H_2 + O_2$ mixture for different initial concentrations (P_1 = 0.097 mmHg, quartz reaction vessel washed with HF, T = 743 K).[19,25]

Expt. No.	P_0, mmHg	η_∞^{expt}, %	P_0/P_1	Expt. No.	P_0, mmHg	η_∞^{expt}, %	P_0/P_1
1	0.103	39	1.06	6	0.133	50	1.33
2	0.099	37	1.02	7	0.103	38	1.06
3	0.095	0	0.98	8	0.099	37	1.02
4	0.099	37	1.02	9	0.095	0	0.98
5	0.160	55	1.65				

The theory of BCP[3] gives the following equation relating the concentration of hydrogen atoms in the isothermal flame of a mixture of H_2 and O_2 to the degree of transformation:

$$\frac{[H]}{[O_2]} = \xi = 2\eta + 2\frac{P_1}{P_0}\ln(1-\eta) \qquad (5)$$

This expression was obtained from the generally accepted scheme for the combustion of hydrogen:

$$OH + H_2 \rightarrow H_2O + H \qquad (I)$$

$$H + O_2 \rightarrow OH + O \qquad (II)$$

$$O + H_2 \rightarrow OH + H \qquad (III)$$

$$H + \text{wall} \rightarrow \text{chain termination} \qquad (IV)$$

and does not take account of changes in the reaction mechanism, the properties of the surface, and the efficiency of heterogeneous chain termination during combustion. In Eqn.(5), the ratio P_1/P_0 replaces the ratio $k_4/2k_2[O_2]_0$, where k_2 and k_4 are the rate constants of reactions (II) and (IV). It is assumed that the value of k_4 remains unchanged during combustion, like the value of k_2.

It can be seen from Eqn.(5) that after combustion, that is when $\xi = 0$, the final degree of transformation is given by the expression

$$\eta_\infty = -\frac{P_1}{P_0}\ln(1-\eta_\infty) \qquad (6)$$

This expression relates η_∞ only to the pressures P_0 and P_1, measured in the same series of experiments and relating to the initial moment of the process. It can be seen from Fig.2 that Eqn.(6) does not describe the large degrees of combustion, nor their abrupt increase immediately above the limit,

The following numbering of the elementary stages of the oxidation of hydrogen is used:

$H_2+O_2\rightarrow 2OH$ (0)
$OH+H_2\rightarrow H_2O+H$ (I)
$H+O_2\rightarrow OH+O$ (II)
$O+H_2\rightarrow OH+H$ (III)
H + wall → chain termination (IV)
$H_{sorbed} + O_2 \rightarrow HO_2$ (V)
$H+O_2+M\rightarrow HO_2+M$ (VI)
$H+HO_2\rightarrow 2OH$ (VII)
$H+HO_2\rightarrow H_2+O_2$ (VIII)
$H+HO_2\rightarrow H_2O+O$ (IX)
HO_2 → chain termination (X)

nor the subsequent marked decrease in the dependence of η_∞^{expt} on P_0/P_1 which takes place in spite of the presence of ten percent of the unreacted substance.

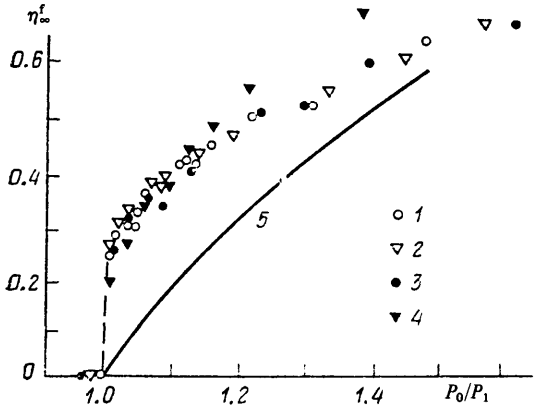

Figure 2. Final degree of transformation at 743 K for a $2H_2 + O_2$ mixture in a quartz vessel with diameter 5 cm, washed with hydrofluoric acid: *1*, *2*) reaction vessel in an assembly with lubricant-free valves, diffusion pump: *1*) oil, *2*) mercury; *3*, *4*) reaction vessel in an ordinary vacuum assembly with lubricated taps, oil diffusion pump; *5*) calculated from Eqn.(6).[23]

The previously accepted ideas about the constancy of the properties and the role of the surface in BCP also do not make it possible to describe the observed development of the chain process with time for all detectable degrees of combustion (Fig.3). It is also possible to compare the observed maximum rate of chain isothermal combustion with the calculated value obtained with the traditional assumption that only chain termination with an unchanged rate "constant" takes place on the surface. It is known that in a system in which combustion has begun, the starting materials are used up practically only in reactions with the chain carrier. Thus in the induction period, that is when the concentration of chain carriers is low, the rate of the process is practically equal to zero (see Fig.1). Thus under combustion conditions, the reaction of H_2 and O_2 molecules with one another can be neglected. The maximum rate of chain combustion is

$$w_{max} = -\left|\frac{d[O_2]}{dt}\right|_{max} = k_2[H]_m[O_2]_m \qquad (7)$$

where t is the time, and $[O_2]_m$ and $[H]_m$ the concentrations of O_2 and atomic hydrogen at the moment corresponding to the maximum rate of the BCP. It is obvious that

$$w_{max} < k_2[H]_{max}[O_2]_0 \qquad (8)$$

where $[H]_{max}$ is the maximum concentration of H atoms, and $[O_2]_0$ the initial O_2 concentration. Eqn.(5) readily gives the following expression for $[H]_{max}$:[19]

$$\frac{[H]_{max}}{[O_2]_0} = \xi_{max} = 2\left(1 - P_1/P_0 + \frac{P_1}{P_0}\ln\frac{P_1}{P_0}\right) \qquad (9)$$

Substituting the value of $[H]_{max}$ from this equation in Eqn.(7) for the conditions of, for example, experiment *3* (Fig.1) ($P_0/P_1 = 1.12$), and using the recommended[30]§ value $k_2 = 2.2 \times 10^{14}_{exp}(-70640/RT)$ $cm^3 mole^{-1} s^{-1}$ gives the calculated value $k_2[H]_{max}[O_2]_0 \cong 10^{13}$ molecule $cm^{-3} s^{-1}$ (that is 7.7×10^{-4} mmHg s^{-1}). From the inequality (8), the discrepancy between experiment and the calculation carried out without allowance for the change in k_{het} during combustion is even greater. There is also a qualitative difference between the dependence of w_{max} on P_0/P_1 observed experimentally and obtained by the traditional calculation.

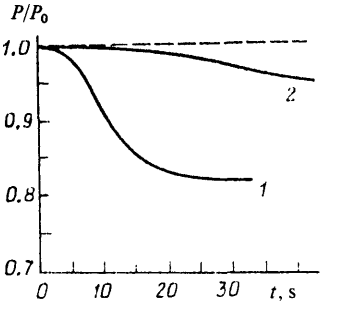

Figure 3. Kinetics of the consumption of O_2 in detonating gas, recorded experimentally (*1*) and calculated using a computer (*2*) according to the reaction scheme (0)–(IV) for a constant k_4 ($P_1 = 0.105$ mmHg). The sections of the curves after the induction periods are given.[29]

An indication that the principal reason for the "anomalies" is to be found in the heterogeneous stages is provided not only by the absence of self-heating and termolecular reactions, but also by the marked dependence of the effect of the anomalies on the material and state of the surface. For example, in reaction vessels from different quartz specimens, differences are observed not only in the ignition limits but also in the final degrees of transformation for a given pressure P_0/P_1.[19,25,31] In a number of other cases, the degrees of combustion are found to be practically identical for appreciably different P_1,[25,31] that is for different initial values of k_{het}. On some surfaces, anomalously high rates and degrees of combustion are not observed, and this does not depend on the value of P_1.

In contrast to the "anomalous" character of the kinetics of the developing combustion and the final degrees of combustion, the behaviour of the system in the induction period is described quantitatively by the familiar[3] expression which does not take account of any change in the value of k_{het} during the process. This also indicates that the factors responsible for the deviation of the kinetics from the linear theory arise during the combustion. Here, as in Refs.19 and 28, the induction period is defined as the time interval from the end of the introduction of the mixture into the reaction vessel to the moment when the greatest curvature is reached on the kinetic pressure curve.

§ Activation energy in J $mole^{-1}$.

Heterogeneous self-acceleration is also observed in the oxidation of CO in the presence of small quantities of H_2.[19,32,33] For example, for a value of $[O_2]_0$ which is 2% greater than $[O_2]_1$, a $2CO + O_2 + 2\%H_2$ mixture under isothermal conditions shows a degree of combustion of 12% (Fig.4), which is several times the value which would be obtained if there were no change in the efficiency of the heterogeneous termination. The anomaly in this case is particularly marked, if account is taken of the fact that in this process there are long chains with infrequent branching,[8,34] and the condition for chain combustion is defined by the inequality

$$2k_2[O_2]\frac{k_3[H_2]}{k_3[H_2]+k_5} \geqslant k_4$$

where k_5 is the rate constant for the heterogeneous disappearance of oxygen atoms. Since the consumption of O_2 and CO is accompanied by the consumption of H_2, which is responsible for the induction, it can be seen from the last expression that if the efficiency of the heterogeneous chain termination remained unchanged, the self-acceleration of the process would not stop until $[O_2]$ became equal to the measured limiting value. As in the case of the examples of the oxidation of H_2 examined above, this process took place isothermally, because of the low pressures and the long combustion times (0.21 mmHg and ~10 s respectively).

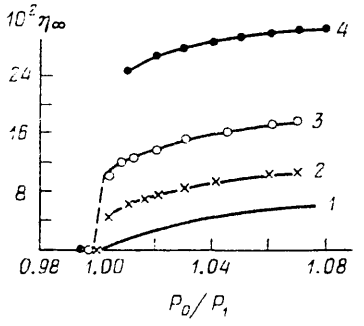

Figure 4. Final degree of combustion of O_2 in a $2CO + O_2 + nH_2$ mixture;[32] *1*) result of the solution of the system of equations for $n = 2\%$; *2*, *3*, *4*) results of the experiment for $n = 1$, 2, and 3% respectively; 723 K.

Heterogeneous self-acceleration is also observed in the branched-chain processes involved in the oxidation of phosphorus vapour[19,21] and silane[22] and the decomposition of nitrogen trichloride.[20,35]

IV. SORPTION OF THE COMPONENTS OF THE REACTION MIXTURE AND ITS ROLE IN COMBUSTION

The adsorption non-uniformity of a solid surface is due to the presence of both defects in the structure of adsorbent and surface compounds of different types. In particular, the surface of quartz under the conditions being considered is hydroxylated to a considerable extent (see for example Refs.36–40), and these hydroxyl groups (isolated or in groups) to a large extent determine the sorption properties of the surface.[36,37] At the temperatures of the experiments on the study of the combustion of H_2, CO, and hydrocarbons, evacuation leads to the partial dehydroxylation of the surface, as shown by the infrared spectra of the surface groups.[36,37] The introduction of water over the surface, however, leads to its rehydroxylation, for example as a result of the opening of siloxane groups.[36,37] The sorption of H_2O does not lead only to the formation of strong hydroxyl bonds "isolated" from one another.[36,37] Under the conditions being considered, water vapour is also extensively chemisorbed on a number of other surfaces used as coatings in kinetic experiments, including B_2O_3;[37] evacuation of the system leads to dehydroxylation of the surface.

Experimental data obtained in recent years show that during chain combustion even at 800–900 K, appreciable adsorption of stable and labile components of the reaction mixture takes place. This obviously influences the properties of the surface. For example, from the stoichiometry of the process

$$2H_2 + O_2 \rightarrow 2H_2O$$

it can be seen that the decrease in the number of moles of the mixture is equal to the number of moles of oxygen reacting.

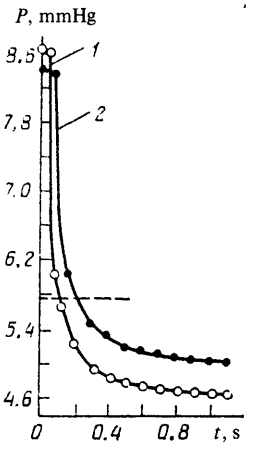

Figure 5. Kinetic curves giving the decrease in pressure during the combustion of a $2H_2 + O_2$ mixture at 923 K over MgO: *1*, *2*) experiments at different initial pressures.[19]

Thus if all the components of the mixture remained in the gas phase, it follows that in a closed volume at the end of the combustion of a stoichiometric mixture, the decrease in pressure should not exceed $^1/_3$ of the initial pressure. It can be seen from Fig.5, however, that, for example, for combustion over MgO the pressure decreases to a much greater extent; the broken line shows the final pressure which would be established for the complete combustion of the mixtures in experiment *1* (Fig.5) if there were no adsorption. Since the pressure of the mixture is lower than the saturated vapour pressure of H_2O, condensation does not take place, and all the additional decrease in pressure is due to adsorption. Special measurements show that during the combustion of H_2 close to the first ignition limit over MgO and over quartz, ~20–30% of the water formed is sorbed.[19,28] This influences the ability of the surface to terminate the reaction chains. The change in the adsorbing power of the surface is obviously accompanied by a change in the conditions of migration of the particles on the surface, that is there is a

change in the specific rate of recombination of the sorbed chain carriers with one another. When a role is played by Hinshelwood's mechanism, this leads to a change in the specific rate of heterogeneous chain termination. Moreover, the decrease in pressure brought about by adsorption leads to an additional change (and in the case being considered, an extensive change) in the coefficients of mass and heat transfer. All this influences the kinetics of BCP.

The adsorption of H_2O vapour on the surface of stainless steel is much weaker. Thus for identical initial conditions and identical values of P_1, the kinetics of combustion are different over MgO and over stainless steel. The extensive adsorption of hydrogen halides formed in the reactions of halogen-containing compounds also influences the efficiency of heterogeneous chain termination.[41]

Special measurements[25] in one of the quartz vessels in which "anomalously" high degrees of combustion were observed showed that the sorption of water vapour beforehand leads not to an increase but to a slight decrease in the extent of combustion.

In a number of processes, rapid sorption of chain carriers, not accompanied by their recombination during the process, also takes place. Thus for example at 400–600 °C, that is at the temperatures of the combustion of H_2, CO, and hydrocarbons, H atoms are rapidly chemisorbed on various surfaces which are often used in kinetic experiments (MgO and various types of technical quartz).[19,25,42] In these experiments, atomic hydrogen was obtained by the dissociation of H_2 on an incandescent tungsten wire and (in some experiments) using a high-frequency discharge. At the heater power used, the rate of chemisorption is limited by the rate of formation of H atoms and is close to the rate of combustion of H_2 with O_2 close to the first ignition limit. In the absence of O_2, some of the atoms remain on the surface for a period of time which is much greater than the time of the combustion of H_2 with O_2. These results are in good agreement with published data on the adsorption of H atoms on the surface of different types of quartz, not accompanied by rapid recombination (see for example Refs.43–47). The adsorption capacity and the rate of adsorption for the MgO surface is tens of times greater than that for the quartz surface.[19,25,42]

It has also been found that molecular oxygen reacts with adsorbed hydrogen atoms.[19,25,42] The characteristic time of this heterogeneous reaction is comparable with the time of combustion of H_2 with O_2 at analogous oxygen concentrations. Since in the experiment with synthetically prepared H atoms the reaction vessel was evacuated before the introduction of O_2, the most strongly chemisorbed H atoms remained on the surface at the start of the reaction. It is obvious that in the experiments on the study of the oxidation of, for example, H_2, some of the atoms adsorbed during the combustion are more weakly attached to the surface and therefore react with O_2 at an even greater rate. Thus some of the chemisorbed hydrogen atoms take part in the chain process, as suggested in Ref.15. The formation of HO_2 radicals in this heterogeneous reaction was observed, for example, in Ref.47. Since, as noted above, under combustion conditions the HO_2 radicals for the most part are involved in reactions in which there is positive interaction of the chains

$$HO_2 + H \rightarrow 2OH$$

it follows that some of the sorbed chain carriers are in fact finally returned to the gas phase, decreasing the efficiency of heterogeneous termination. Thus the mechanism proposed in Refs.15 and 16 has been confirmed experimentally in a number of studies.

The reaction of O_2 with adsorbed H atoms is of course not the only process altering the properties and role of the surface during combustion. At the same time, in addition to heterogeneous self-acceleration, it is the reactions of sorbed atomic hydrogen that led to the after-effect of combustion of H_2 in the oxidation of CO, in spite of the fact that the reaction vessel was evacuated before the introduction of the mixture of CO and O_2.[19,48] Direct experiments proved that the observed strong after-effect is not due to a trace of the molecular component; the introduction of H_2 and even H_2O into the reaction vessel with subsequent evacuation for the same time interval does not influence the combustion of carbon monoxide. On the other hand, treatment of the surface with the flame of a "dry" mixture of CO and O_2, in the course of which mainly oxygen atoms "disappear" on the surface, raises the first ignition limit of hydrogen.[11] Thus the inverse relationship between the state of the surface and the gas-phase process in this case is revealed in the fact that different BCP influence one another as a result of a change in the properties of the surface, which shows a "memory effect".

In a number of BCP taking place at temperatures which are not too high, an important role is also played by the adsorption of the starting materials. One such process is the oxidation of phosphorus vapour (P_4). Studies of this reaction have played an important part in the development of the theory of branched-chain processes. At the same time, the regular features and mechanism of this reaction have not been fully investigated. As in the study of other BCP, until recently no account was taken of possible changes in the state of the surface and change in the efficiency of heterogeneous chain termination. It has been shown experimentally[19,21,49] that under the conditions of the usual experiment with P_4 vapour, extensive adsorption of the vapour on the walls of the reaction vessel and connecting tubes takes place (the saturated vapour pressure is $\sim 2.5 \times 10^{-2}$ mmHg at room temperature). It has also been shown that the destruction of the chain carriers takes place 10^2–10^4 times more intensely on adsorbed phosphorus than on glass and quartz.[11,50] It may be noted that it was because of this previously unrecognised change in the efficiency of heterogeneous chain termination, characteristic of the usual experiment with phosphorus vapour, that the first ignition limit was sufficiently high to be detected and studied in classical experiments.[1,51,52]

EPR has shown[21,53] that during the combustion of P_4 vapour, appreciable quantities of P atoms and phosphorus–oxygen radicals are adsorbed on the walls of the reaction vessel and do not recombine. This to a large extent determines the stoichiometry of the overall gas-phase process. The quantities of these atoms and radicals "condensed" in the matrix of sorbed phosphorus vapour and other components of the mixture change during the combustion. When the combustion process is carried out in a stream, the composition of the sorbed intermediate products changes along the stream.

The influence of sorbed phosphorus on the kinetics of the combustion is shown particularly strongly under conditions when the surface is not completely covered by the adsorbate. Since the adsorbed phosphorus is used up in the reaction with the chain carriers, the efficiency of chain termination decreases during the combustion. Thus under these conditions, anomalously high rates of the process and degrees of combustion are observed.[19,21] The results of one of the experiments are illustrated in Fig.6. P_4 was introduced into an evacuated reaction vessel to give a stationary pressure of 2×10^{-3} mmHg (which is 12 times lower than the saturated vapour pressure over solid white phosphorus). It is obvious that at this low pressure, the surface concentration of adsorbed phosphorus present in equilibrium with the gas phase is also low. When the given P_4 vapour pressure had been established, O_2 was introduced slowly into the

reaction vessel. When the pressure of the mixture reached 4.87×10^{-2} mmHg, the subsequent addition of O_2 was carried out in portions (δ). The pressure of each portion was 2×10^{-4} mmHg. Fig.6 shows that the time intervals between the O_2 supply pulses was 1 min, which is much greater than the ignition induction period. It can be seen from Fig.6 that, for example, in the given series of experiments at 4.98×10^{-2} mmHg, the mixture is under the limit, so that there is no ignition. When the next portion of O_2 is added, the mixture is above the limit, and self-ignition takes place. During combustion under the conditions being considered, there is no homogeneous positive interaction of the chains or self-heating.[19,26] At the same time, Fig.6 shows that the quantity of the mixture which has undergone combustion is ~15 times the quantity of O_2 introduced into the reaction vessel in the last portion, that is the degree of combustion is greater by an order of magnitude than the amount by which O_2 initially exceeds the ignition limit in the given experiment. The maximum rate of the chain combustion is also "anomalously high".

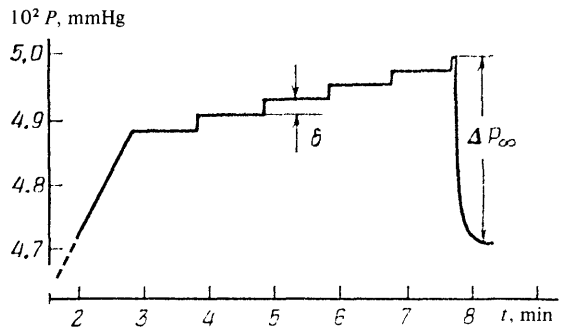

Figure 6. Kinetics of the change in the pressure of P_4 vapour and O_2 for the pulsed introduction of small portions of O_2 into a reaction vessel whose surface was impoverished in phosphorus.[21]

In recent papers,[54-57] the same authors tried to deny that a change in the state of the surface takes place during combustion; these authors state that the "anomalously high" degrees of combustion during the oxidation of H_2 result from the action of some inhibitor liberated from the vacuum lubricant of the taps. The data given in the works cited show, however, that the authors did not evacuate the assembly sufficiently after washing and lubricating the taps, so that the solvent sorbed in the lubricant was desorbed into the reaction vessel; the oscillograms given in Ref.56 show that in the closed reaction vessel in contact with the taps, the pressure increases at a constant temperature, in spite of the fact that in the reaction of H_2 with O_2 the number of moles decreases. This represents a fundamental difference between the experiment in Refs.54–57 and the experiments of all other authors, carried out at the same manometer sensitivity (for example Refs.17, 19, and 25). The introduction of a foreign substance into the reaction vessel in the experiments[54-57] and its inhibiting action are due mainly to the fact that in Ref.56, when the side-arm of the reaction vessel was cooled with liquid nitrogen, the mixture, which was initially under the first self-ignition limit, ignited. These results obviously have no relation to studies by other workers, carried out observing the generally accepted precautions for preventing the introduction of foreign substances into the reaction mixture.

Special experiments[23] showed that with the usual sufficiently thorough evacuation of the assembly, carried out after lubricating the taps, cooling the side-arm of the reaction vessel does not lead to the ignition of a mixture which is directly under the first limit. Moreover, Fig.2 shows that when the familiar requirements of the procedure are fulfilled, the degree of the observed "anomaly" in a given reaction vessel is independent of whether the reaction vessel is in an assembly with metallic lubricant-free valves (open circles and triangles) or in the ordinary apparatus for kinetic experiments with lubricated vacuum taps (black circles and triangles). The same is true of P_1 and the induction period. The results of the measurements coincide, irrespective of whether the connections in front of the intermediate volume are cooled with liquid nitrogen (open circles) or not cooled (open triangles), and also of whether the evacuation is carried out with an oil or a mercury diffusion pump.[23]

In Ref.56, a series of experiments was carried out with continuous cooling of the side-arms of the reaction vessel with liquid nitrogen to prevent the introduction of foreign substances from the insufficiently evacuated lubricant of the taps into the reaction vessel. The oscillograms given show that in all these experiments, the observed maximum rates of the process were appreciably greater (from two to twelve times greater) than the calculated values obtained without allowance for the change in the properties of the surface, that is the reaction rates were "anomalously high" even in those experiments of Ref.56 which the authors called clean. This fact was not noted in Refs.54–56.

It should be specially emphasised that in all the studies, the procedure used in the experiments to detect the "anomalous" kinetics of chain processes, and the vacuum assemblies used, are standard; this procedure and these assemblies have always been used and are still being used to study gas-phase chain processes. In particular, using this procedure and under the same conditions (including the same pressures) as in Refs.19, 23, 25, 29, and 54–57, different authors have determined the principal characteristic features of the first self-ignition limit of mixtures of H_2 with O_2, as a model BCP (see for example Refs.3–5, 10, and 58–60). Thus the assertion in Refs.54–57 that the vacuum lubricant has a distorting influence applies not only to the "anomalies" but also (and particularly) to the generally accepted procedure for studying BCP and to all their familiar regular features, previously established by different workers. As shown above, this assertion by the authors cited,[54-57] which categorises the generally accepted procedure and all the results obtained using it as erroneous, results from the fact that they attribute to the work of other authors the lack of thorough preparation of the assembly for the experiments which was shown in the works cited.

It is obvious that if some impurity had been introduced into the reaction vessel from the vacuum lubricant and had influenced the chain reaction when the usual precautions for ensuring the purity of the reaction mixture had been taken, then a large number of facts would not have been observed—the reliably established characteristic regular features of BCP, familiar from courses of chemical kinetics and from monographs. Examples of these regular features are: the marked dependence of P_1 on the material and the state of the surface of the reaction vessel;[2-6,59] the inverse relationship between the value of P_1 and the diameter of the reaction vessel, including that in the kinetic range of chain termination;[10,58,60] the quantitative agreement between

theory and experiment in the method for controlling ignition by means of metal rods;[4,10] etc.

V. KINETIC MODELS OF THE HETEROGENEOUS SELF-ACCELERATION OF BRANCHED-CHAIN PROCESSES AND A NEW TYPE OF FLAME PROPAGATION

On the basis of data obtained in the study of BCP, including the investigation of the nature of the heterogeneous reactions of the chain carriers and the mechanism of the decrease in the efficiency of termination on the surface, two principal types of kinetic scheme corresponding to the heterogeneous self-acceleration of various processes of chain combustion have been proposed.[19,29] These schemes explain both the ignition limits and the induction periods, and also the kinetics of combustion, including the dependence of the "anomalous" values of w_{max}^{expt} and η_{∞}^{expt} on the initial conditions. Analysis of these schemes shows, in particular, that on a number of surfaces under certain conditions, there is non-uniformity of the stationary states, and this is responsible for the critical phenomena within the ignition range, detected, for example, in Refs.19, 23, 25, 32, and 61.

The first of these reaction schemes takes account of the reactions of the gas-phase components with sorbed atoms and radicals and the subsequent positive interaction of the chains. In the case, for example, of the model BCP of H_2 oxidation, and also the combustion of a number of hydrogen-containing compounds, allowance for the reaction of O_2 with the sorbed H atoms and the reactions of the HO_2 radicals formed, suggested in Refs.15 and 19, leads to the following expression for the effective rate constant of heterogeneous chain termination:

$$k_{het} = k_{het}^0 \left[1 - \beta \frac{k_7 [H]}{(k_7 + k_8 + k_9)[H] + k_{10}} \right] \qquad (10)$$

where k_{het}^0 is the rate of the capture of atomic hydrogen by the surface at unit concentration of these particles in the gas phase (specific rate); β the fraction of sorbed H atoms forming HO_2 radicals with O_2; and k_7, k_8, k_9, and k_{10} the rate constants of the above reactions (VII)–(X) respectively.

Outside the ignition range, and also before the start of the combustion (in the induction period), when the quantity of H atoms is very small, the expression in square brackets in Eqn.(10) is practically equal to unity, so that

$$k_{het} = k_{het}^0$$

Thus in this case the adsorbed H atoms do not influence the efficiency of the heterogeneous termination. During the developed combustion, however, as a consequence of the marked increase in the concentration of atomic hydrogen, the value of k_{het} decreases, as can be seen from Eqn.(10), and tends to its limiting value:

$$k_{het}^c = k_{het}^0 \left(1 - \beta \frac{k_7}{k_7 + k_8 + k_9} \right) \qquad (11)$$

The superscript "c" indicates that the value relates to combustion conditions.

This decrease in the effective rate constant of the heterogeneous chain termination during combustion obviously leads to an additional sharp increase in the rate of the chain process, the concentrations of the chain carriers, and the final degree of transformation, as observed experimentally by the present author in the form of the "anomalies" (for example in Fig.2). Under given conditions, including given concentrations of O_2 and H in the gas phase, the fraction of sorbed hydrogen atoms capable of leading to the formation of HO_2 and to the development of chains depends on the material of the surface. This explains the fact that the extent to which the quantitatively reproducible regular features deviate from those expected on the basis of earlier ideas, that is the magnitude of the "anomalies", depends on the material of the surface¶.

Allowance for the heterogeneous development of the chains also makes it possible to explain the observed sharp decrease in the dependence of the maximum rate and degree of transformation on P_0 when the initial pressure increases above a certain value (see for example Figs.2 and 4). In fact, since the maximum concentrations of the chain carriers usually increase sharply with increase in P_0 and on passing through the first ignition limit, it follows that when the initial pressure is even only slightly greater than P_1, H atoms are formed during combustion in such large quantities that there is an appreciable decrease in k_{het} by the mechanism described above. There is a correspondingly anomalous sharp increase in the values of w_{max}^{expt}, η_{∞}^{expt}, and $[H]_{max}$. At the same time, because of the appreciable concentrations of H atoms even at values of P_0 which are only 1–2% greater than P_1, the constant k_{het} may reach its limiting value defined by Eqn.(11). It is obvious that in this case, with further increase in P_0 in each given experiment, the value of k_{het} will decrease to the above same limiting value, that is by the same amount. As a consequence of the sharp increase in the concentration of chain carriers on ignition, the decrease in k_{het} is complete in the earliest stages of the combustion, and the subsequent chain process proceeds to completion with a new decreased heterogeneous termination rate "constant", equal to k_{het}^c.

There are thus two stable values of k_{het}: one under stationary conditions, equal to k_{het}^0, and another under combustion conditions, given by Eqn.(11). Above a certain initial pressure P_0^* lying in the ignition range, for all values of P_0 the chain combustion takes place with the same stationary value of the heterogeneous termination rate "constant", k_{het}^c, which is much smaller than the initial value k_{het}^0. Since no further decrease in k_{het} takes place with increase in P_0 above P_0^*, the "anomalously" marked increase in η_{∞}^{expt}, w_{max}^{expt}, and $[H]_{max}$ also stops. This means that the dependence of these quantities on P_0 above the initial pressure P_0^* indicated in the absence of other heterogeneous reactions and self-heating should be described, with an accuracy corresponding to the correction for the contribution of the reaction

$$O + OH \rightarrow O_2 + H \qquad (II')$$

by Eqns.(6), (8), and (9), in which, however, the measured value of P_1 is replaced by the value corresponding to the new established value of k_{het}^c.

In fact, it is known that[2-6,59]

$$P_1 = k_{het}/2k_2\gamma_{O_2} \qquad (12)$$

where γ_{O_2} is the mole fraction of O_2. It is therefore obvious that the decrease in k_{het} to k_{het}^c leads to a corresponding lowering of the ignition limit to P_1^c, and the actual abscissae of the measured η_{∞}^{expt} are not P_0/P_1, but P_0/P_1^c. For example, in Fig.7 the experimental dependence of the degree of transformation on P_0/P_1 shows a break at $\eta_{\infty}^{expt} = 0.38$.

¶The reactions of the chains of the type (VII) and (VIII) may involve both desorbed HO_2 radicals and HO_2 radicals situated on the surface. In the general case, therefore, Eqn.(10) contains another negative fraction, analogous to that given, which also increases to its limiting value with increase in the concentration of H atoms during the combustion.

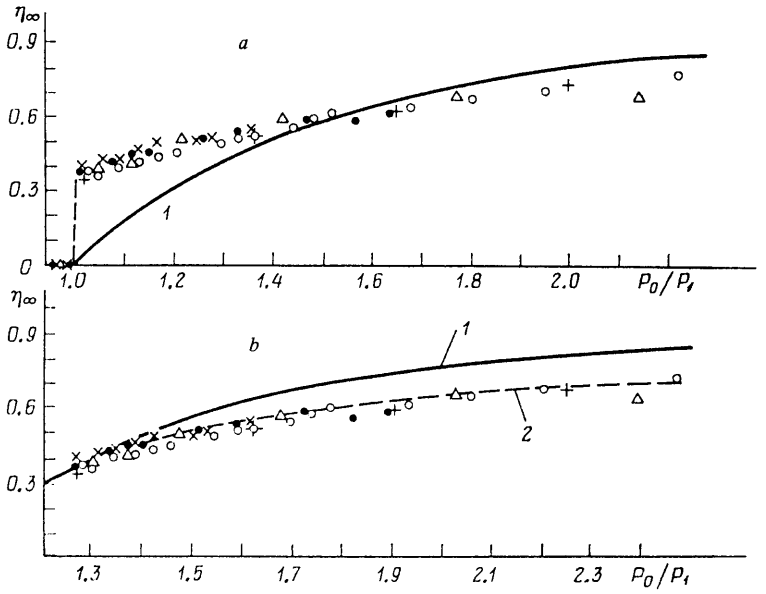

Figure 7. *a*) Change in the degree of transformation of O_2 with change in P_0/P_1 in different series of experiments at 723 K (different point symbols) and the results calculated from Eqn.(6) (curve *1*); *b*) the same data with the values of P_0/P_1 replaced; curve *2*—result of the computer solution of the system of kinetic equations corresponding to reactions (0)–(IV), (II').[19]

According to Eqn.(6), this degree of combustion corresponds to the ratio $P_0/P_1^c = 1.27$ (see curve *1* in Fig.7), which is 25% greater than P_0/P_1 obtained by dividing the initial pressure by the measured value of P_1, that is during the combustion, the values of k^c and P_1 decrease by 25%. Thus by increasing the abscissae of the measured η_∞^{expt} by 25%, it can be shown that all the experimental data lie on the calculated curve obtained by using a computer to solve the system of equations corresponding to the set of stages (0)–(IV) and (II') (broken line and all the experimental points in Fig.7*b*). This calculation was carried out using the published[30] rate constants of the homogeneous stages; the values of k_4 and k_4^c were determined from P_1 and P_1^c using Eqn.(12).

The mechanism of the heterogeneous reactions, examined above, and Eqn.(10), show that k_{het} may decrease even when the specific rate of the capture of these particles by the surface, that is k_{het}^0, does not decrease. The explanation for this may be that the "anomalously" high values of η_∞^{expt} and w_{max}^{expt} are also observed for various surfaces on which the adsorption of the chain carriers takes place in the diffusion range (MgO, stainless steel[19,28,61,62]). Fig.8, in addition to the experimental data of Ref.61, also gives the results of a computer calculation carried out in Ref.63 for the initial conditions of the experiment with allowance for self-heating, termolecular reactions, and homogeneous interaction of the chains, but without allowance for the change in the efficiency of the heterogeneous chain termination. The different calculated curves in Fig.8 correspond to change in the values of the parameters used. The broken calculated curve was obtained using an increased (relative to the recommended value[30]) value of the rate constant of stage (VI). For this value of k_6, the calculated second ignition limit was found to be less than half the measured values. It can be seen that for P_0 only slightly greater than P_1, the observed degrees of combustion are much greater than the calculated values. Moreover, in contrast to the results of the calculation,[63] the experimental curve shows a sharp abrupt increase in η_∞^{expt}, which also stops suddenly with increase in P_0, in spite of the fact that tens percent of the original mixture remain unreacted. Allowance for the reaction of O_2 with adsorbed H atoms makes it possible to explain the observed sharp changes in η_∞ with change in P_0/P_1 (as in the case where the process takes place over a quartz surface). For identical initial conditions and equal values of P_1, the kinetics of the combustion and the degrees of transformation are different over MgO and over stainless steel.[19] The characteristic features of combustion over MgO and over stainless steel, and the role of the non-stationary nature of the surface under these conditions, have been examined in detail.[19,64] In addition to the extensive chemisorption, noted above, of water vapour on the MgO surface during the combustion of hydrogen-containing compounds, which has a marked influence on the properties of the surface, rapid chemisorption of atomic hydrogen also takes place under these conditions. It has been noted[65] that the H atoms obtained by a discharge in H_2 reduce MgO, and in the presence of O_2 the following reactions take place:

$$Mg^{++}O^{2-}Mg^{++} \rightarrow Mg^{++}OH^-Mg^+$$
$$Mg^+ + O_2 \rightarrow Mg^{++}O_2^-$$
$$Mg^{++}O_2^- + H_2 \rightarrow Mg^{++}OH^- + OH$$
$$2Mg^{++}OH^- \rightarrow Mg^{++}O_2^{--}Mg^{++} + H_2O$$

in which the hydroxyl radical is formed.

A number of authors have reported the reduction of quartz by atomic hydrogen (see for example Refs.66 and 40), in agreement with the data of Refs.19 and 42.

The development of the chains and a change in the properties of the surface can obviously be brought about by heterogeneous reactions involving species other than atomic hydrogen. There are examples of oxidation involving oxygen present in a chemical compound in the solid phase (see for example Refs.66–69), including O^- radical-anions. Heterogeneous chain termination in other BCP can also be described by equations analogous to Eqns.(10) and (11).

In many cases, the sorption of a gaseous component leads to structural changes in the layer next to the surface, and to phase transformations;[64,70-72] this in turn influences the kinetics of the heterogeneous stages.

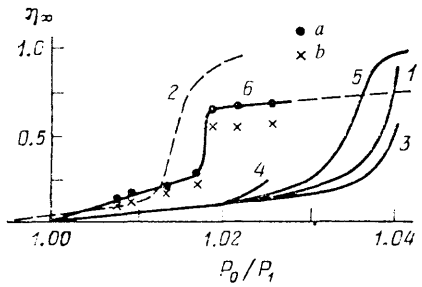

Figure 8. Comparison of the results of the calculation in Ref.63 (curves *1*–*5*) and the experiment in Ref.61 (points and curve *6*); T = 853 K, stainless steel vessel; curves *1*–*5*—calculation for different varying combinations of the rate constants; curve *2* (broken line) was displaced to the left along the abscissa by the authors of Ref.63; the points give the experimental data (*a*—with a correction for the volume of the connecting tubes,[31] *b*—results of the measurements without this correction).

In the theory of chain processes it has been assumed that in the absence of reactions involving interaction of the chains, the change in the concentration of active centres (n) with time (t) is described by the equation

$$\frac{dn}{dt} = w_0 + (f - g)n \qquad (13)$$

where w_0 is the rate of the chain initiation, and f and g the rates of chain branching and termination for unit concentration of the chain carriers (that is the coefficients of linear branching and termination of the chains respectively); f and g have been regarded as being independent of n.

With allowance for Eqn.(11), the equation describing the changes in the concentrations of the carriers with time is obtained in the form

$$\frac{dn}{dt} = w_0 + (f - g_0)n + \frac{an^2}{1 + bn} \qquad (14)$$

where a and b are the combinations of the quantities k_1, k_2, k_3, and β, and $g_0 \equiv k^0_{het}$. Unlike Eqn.(13), Eqn.(14) is non-linear with respect to n; at the same time the presence in eqn.(14) of a positive term in which the power of the quantity n is greater than unity indicates that a sufficiently high concentrations of the chain carriers in the volume or on the surface, the first ignition limit depends not only on the relationship between f and g_0 but also on the concentrations of the chain carriers and on the ratio of the parameters characterising the heterogeneous development of the chains and the reversible changes in the properties of the surface.

From Eqn.(14) it follows, in particular, that it is possible to lower the first ignition limit by artificially increasing the rate of initiation or by the preliminary adsorption of chain carriers. This conclusion has been confirmed experimentally: the preliminary adsorption of H atoms on magnesium oxide and on quartz leads to the quantitatively reproducible lowering of the first ignition limit in the reactions of H_2 with O_2 and of CO with O_2.[11,19,32,73] The quantitative reproducibility of the results shows that in this case also, the change in the properties of the surface under the influence of active intermediate species is reversible. As noted in Refs.19 and 32, in the combustion of CO the heterogeneous development of the chains may involve O atoms in addition to H atoms. The development of chains involving heterogeneous reactions of free atoms and radicals has also been detected in the branched-chain processes involved in the oxidation of silane[22] and phosphorus vapour[19,29] and the decomposition of NCl_3.[19,20]

Heterogeneous reactions of intermediate species, leading finally to chain development, may also play an important role in flame propagation. For example, it can be seen from Eqn.(14) that dn/dt increases with increase in n more rapidly than according to a linear law; this makes possible the non-thermal propagation of the combustion zone.

A number of studies of the decomposition and degenerate-branched oxidation of organic compounds (for example Refs.47 and 74–76) have shown that the adsorbed fragments of the molecules, reacting with O_2, form peroxy radicals which are transferred to the gas phase. In particular, atomic hydrogen, sorbed on the surface of the reaction tube during the decomposition of peroxyformic acid, reacts with O_2 from the gas phase to give HO_2 radicals. These radicals are removed from the reaction zone by the gas stream; they can be condensed by cooling and detected by EPR.[74] The mechanism proposed[76] for the decomposition of peroxyacetic acid includes the reaction of O_2 with adsorbed CH_3 radicals, leading to the partial removal of the methyl peroxy radical into the gas phase. This reaction, which is the analogue of the proposed[15,16] reaction of O_2 with adsorbed hydrogen atoms, also leads to heterogeneous chain initiation. The formation of OH radicals as a result of the reaction of O_2 with sorbed H atoms has been reported.[72,77,78] In these studies, the atomic hydrogen was obtained by an electric discharge in H_2.

The authors of Refs.38 and 79, who detected the reactions of sorbed methyl radicals with gas-phase components during the thermal decomposition of organic compounds over quartz and over MgO, explain the observed regular kinetic features of the chain process on the basis of a reaction scheme which also includes heterogeneous chain development. In a number of studies, the reaction of sorbed hydrogen atoms with deuterium from the gas phase has been observed (see for example Refs.44 and 79). The need to take account of the change in the efficiency of heterogeneous chain termination has also been pointed out in Refs.80 and 81.

The reactions of sorbed chain carriers must apparently be responsible for the observed[22] unique character of the kinetics of the combustion of silane with oxygen in a closed volume close to P_1, shown in Fig.9. It can be seen that the duration of the chemiluminescence after the attainment of the intensity maximum is ten times that before the maximum. It is difficult to attribute this almost constant (and low) rate of combustion to some negative interaction, since it is known[82,83] that in this process, on the contrary, an important role is played by the positive interaction of the chains. An unambiguous indication of this is provided by the observed[82] non-thermal propagation of the flame in a gas mixture outside the self-ignition range. Thus in the kinetics of combustion shown in Fig.9, heterogeneous chain development is probably of considerable importance. This is also indicated by the conditions of double ignition of a mixture of silane with O_2 in a closed volume, which depends on the previous treatment of the surface by the flame.[22,82]

In another type of heterogeneous process leading to "anomalous" self-acceleration of BCP and to non-uniformity of the stationary states, the principal factors are the non-uniformity of the surface and the disappearance of its active

sites during chain combustion. A specific example of a process of this kind is provided by the oxidation of phosphorus vapour.[29] For simplicity it is assumed that the heterogeneous chain termination is determined by only two types of surface: regions occupied by phosphorus, on which termination is very effective,[19,21] and regions free from phosphorus. In this case, the effective rate constant of the termination is given by the expression:

$$k_{het} = k_f + (k_o - k_f)(1 - b_0)\exp\left(-k\int_0^t n\,dt\right) \qquad (15)$$

where k_0 and k_f are the rate "constants" for termination on the active (occupied by phosphorus) and inactive (free) regions of the surface, b_0 the fraction of the inactive part of the surface at the start of ignition, and k the rate constant for the disappearance of the active sites of the surface (in this case the consumption of sorbed phosphorus).[29] It can be seen from Eqn.(15) that there are two stationary values of k_{het}: in the absence of combustion (before the start of the combustion or outside the ignition range), that is for $t = 0$ and $n = 0$, the value is

$$(k_{het})_{t=0} = k_o(1 - b_0) + k_f b_0 \qquad (16)$$

Under conditions where combustion has begun, however, as a result of the rapid increase in n, the value of k_{het} decreases sharply, tending in the limit to $(k_{het})_\infty = kf$. This decrease in the efficiency of heterogeneous chain termination obviously leads to additional self-acceleration of the chain process and to the "anomalously" high degrees of combustion observed experimentally.

If the rate constant k_f in Eqn.(15) is denoted g_0, and the product of the differences in front of the exponent by α, and if account is taken of the fact that k_{het} is represented by g in Eqn.(13), the latter can be written in the form

$$\frac{dn}{dt} = w_0 + \left[f - g_0 - \alpha\exp\left(-k\int_0^t n\,dt\right)\right]n \qquad (17)$$

Unlike Eqn.(13), Eqn.(17) is non-linear with respect to n, and, like Eqn.(14), it shows that the critical conditions for self-ignition depend on the concentration of chain carriers. Correspondingly, BCP may show kinetic features characteristic of processes with homogeneous positive interaction of the chains. Eqn.(17), like Eqn.(14), shows, in particular, that it is possible to have non-thermal propagation of the flame, brought about by a decrease in the efficiency of heterogeneous chain breaking ahead of the combustion front under the influence of the reaction chain carriers. This phenomenon was in fact detected by the present author; in a mixture of P_4 vapour and O_2 present in a long tube at a pressure under the first self-ignition limit, an isothermal flame passes along the tube if a small spark is produced at one end.[84] Special experiments showed that under these conditions there is no homogeneous interaction of the chains, and the regular features of the propagation of the flame depend on the material and state of the surface.[21,26] In these experiments, the quantity of adsorbed phosphorus was small, because of the low partial pressure, lower than the saturated vapour pressure.

The phenomenon of non-thermal "heterogeneous" propagation of a flame may also obviously take place in other BCP. In the more general case, a change in the efficiency of heterogeneous chain termination under the influence of chain combustion may lead to a change in the rate of propagation or to a change in the length of the combustion zone in the stream. In view of what has been said above, the rate "constant" for heterogeneous chain termination, appearing in the equation describing the propagation of the flame, depends not only on temperature but also on the concentration of chain carriers.

The dependence of the rates of branching (*1*) and termination (*2*) on the concentration of active intermediate products in the heterogeneous development of the chains and the passivation of the surface (the cases to which Eqns.(14) and (17) respectively relate) is given in Fig.10. At values of n greater than the abscissa of the second intersection of the curves or the point of tangency of the curves, chain branching predominates over termination, to an extent which is greater, the larger n becomes. This leads to self-ignition of the mixture, non-thermal propagation of the flame, etc. If the termination graph lies below the straight line *2'*, the mixture undergoes self-ignition for all values of n.

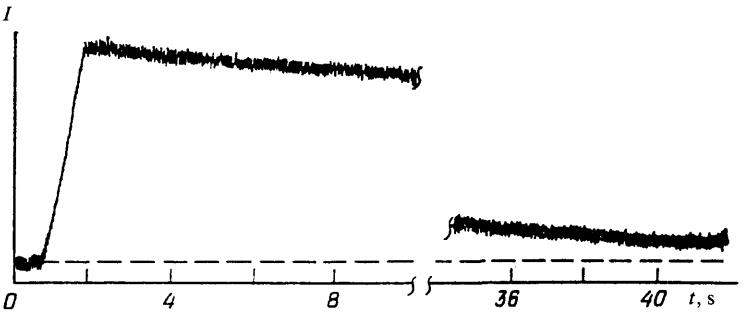

Figure 9. Oscillograms showing the change in the chemiluminescence during the combustion of silane in the mixture: 8% SiH_4 + 76.5% O_2 + 15.5% He; T = 473 K, P_0 = 0.96 mmHg.[22]

A mathematical description has been given[85] for the non-thermal propagation of a flame, brought about by the decrease in the efficiency of heterogeneous chain rupture ahead of the reaction front.

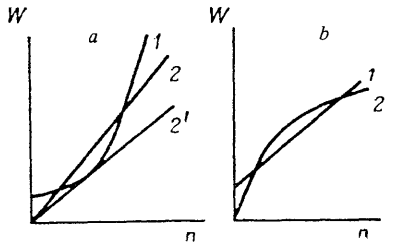

Figure 10. Rates of branching (*1*) and termination (*2*) in the cases corresponding to Eqns.(14) (*a*) and (17) (*b*).[29]

VI. PULSED CHAIN COMBUSTION AND THE NON-STATIONARY NATURE OF THE STATE OF THE SURFACE

A characteristic manifestation of the inverse relationship between the kinetics and mechanism of the heterogeneous reactions of chain carriers and gas-phase BCP is the condition of repeated self-ignition in a closed volume close to the first limit, which has been detected and studied for the decomposition of NCl_3 [19,20] and the oxidation of carbon monoxide,[18,19,48] silane,[22,82] and phosphorus vapour.[19,21,26,49] In most experiments, the concentrations of the reagents were very low, and ignition was not accompanied by self-heating.

The pulsed combustion of, for example, hydrocarbons and CO was also observed earlier.[86] The pressure of the mixture was several hundred mmHg, however, and the process was accompanied by considerable self-heating of the mixture. On this basis, the periodic ignition in the closed volume was related to the self-heating.[86-88] It is not excluded that under certain conditions, self-heating is in fact one of the necessary conditions for repeated ignition.[89,90] It cannot be assumed, however, that self-heating is necessary for pulsed conditions in all cases. Close to the first ignition limit, the regular features of the pulsations are determined to a large extent by the dependence of the reactions of the sorbed chain carriers, the desorption of the molecular reagents, and the change in the efficiency of the heterogeneous termination on the nature of the surface and on the type of BCP. In the oxidation of CO and P_4 vapour and the decomposition of NCl_3, the number of ignitions for a single introduction of gas into the reaction vessel may be greater than 50, depending on the initial conditions, including the quantity of sorbed chain carriers.

The decisive role of chemisorbed chain carriers in, for example, the pulsed combustion of CO over an MgO surface was shown by the following experiment.[48] It was established that when the ignition of a "dry" mixture of CO and O_2 was carried out repeatedly, the number of pulsations decreased from one experiment to another. Since the concentration of the original reagents and the other conditions remained unchanged in all the experiments, the marked decrease in the number of pulsations was due to the change in the properties of the surface. The introduction into this reaction vessel of H_2, water vapour (the original promoters), CO_2 (the combustion product), or a mixture of H_2 and O_2 at a pressure below its first ignition limit, with subsequent evacuation, led to practically no increase in the number of ignitions of the $2CO + O_2$ mixture introduced into the reaction vessel after the evacuation. If however two or three ignitions of H_2 with O_2 were carried out in this "exhausted" reaction vessel, then after evacuation the picture of repeated ignition of CO was restored. This shows that intermediate combustion products, that is hydrogen atoms, are chemisorbed on the surface, remain partly on the surface after evacuation, and subsequently lead to the repeated ignition of the mixture of CO and O_2 when it is introduced into the reaction vessel.

The pulsed combustion of CO over, for example, MgO is explained as follows.[19] As shown by EPR spectroscopy,[11,91] in the combustion of CO in the presence of hydrogen or water vapour under the given conditions, tens percent of H_2 (H_2O) are present as atoms and radicals. An appreciable proportion of the latter disappear on the surface. As noted above, there is considerable chemisorption of H atoms during combustion. As a result, there is a decrease in the concentration in the reaction mixture of hydrogen (or water), which acts as the initiator of the given chain reaction; as a result, the combustion stops. After some time, the initiator is returned from the wall into the volume (as H_2 or H_2O molecules), and when its concentration exceeds the critical value, the mixture ignites again. Since some of the O_2 and CO are used up in each ignition, the pulsations are gradually quenched.

Under certain oscillation conditions, the intensity of the ignitions passes through a maximum with increase in their sequence number.[19,20,21,92] The explanation given in Ref.19 for this regular feature was based on allowance for the changes in the ignition period, the quantity of desorbed reagent (starting material, inductor, etc.), and the properties of the surface. The conclusions reached[18,19] about the important role of the reversible non-stationary nature of the properties of the surface under pulsating CO combustion conditions agrees with the fundamental ideas in later papers.[80,81,93,94]

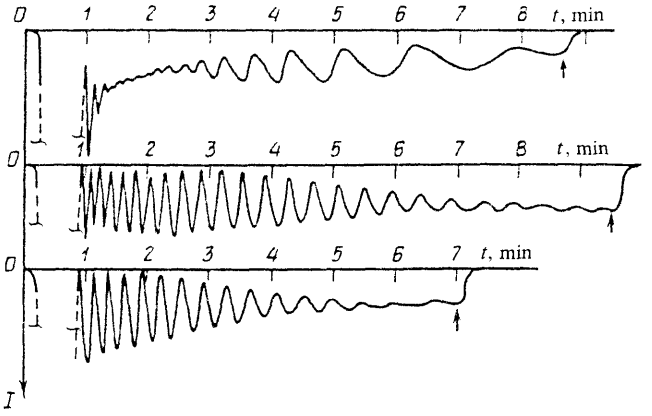

Figure 11. Repeated ignition of NCl_3 in a mixture with helium over different surfaces; the arrow indicates the moment of evacuation.

The active role of the non-stationary state of the surface (primarily as a result of the change in the concentration of chain carriers sorbed on it) under pulsating conditions is also indicated directly by data on the oxidation of silane.[22,83]

This chain reaction shows reversible changes in the properties of the surface, which have a marked influence on the course of the BCP, the "memory effect" of the surface, and hysteresis.

Fig.11 gives oscillograms showing the change in the intensity of the absorption of light (at a wavelength of 248 nm) by nitrogen trichloride under conditions of repeated ignition in a closed volume over NaCl. The increase in the concentration of NCl_3 between ignitions was due to its desorption. The difference in the pulsation conditions in different experiments was due to the fact that the preliminary treatment of the surface, including its treatment by the reactions of the chain carriers, was carried out in different ways.[20] The observed change in the period of the fluctuations and the extent of the combustion on the first oscillogram shows that the efficiency of the heterogeneous chain termination decreases during ignition.

In the study of BCP pulsed conditions, an extremely fruitful approach is to analyse mathematical models of the reactions using, in particular, the methods of stability theory, if account is taken of the reactions of the sorbed chain carriers in the analysis of the phase trajectories;[19] for this purpose, at least one of the axes of the phase space must be assigned to these sorbed species.

VII. HETEROGENEOUS SELF-RETARDATION OF BRANCHED-CHAIN PROCESSES

On a number of surfaces, as a result of heterogeneous reactions of the components of the reacting mixture, the efficiency of chain termination may increase (in contrast to the decrease described above).[29,96] In this case, the values of the rates and the final degrees of combustion reproduced quantitatively in the experiment are lower than the values calculated from the linear theory, that is they are "anomalously" low. This heterogeneous self-retardation has been detected[25,95] for the combustion of detonating gas over NaCl and over alkaline $K_2B_4O_7$.

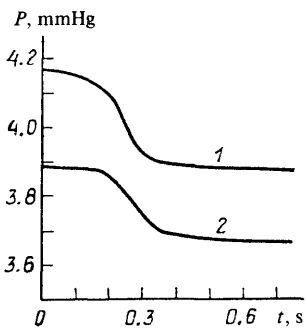

Figure 12. Oscillograms showing the change in the pressure of a $2H_2 + O_2$ mixture over NaCl in two experiments with different initial partial pressures of oxygen $P_0(O_2)$ equal to 1.39 mmHg (curve *1*) and 1.29 mmHg (curve *2*); P_1 = 3.19 mmHg.

Fig.12 gives as examples oscillograms showing the change in the pressure of the mixture with time in two experiments of one of the series at 787 K (quartz vessel with diameter 5.2 cm, covered with sodium chloride). The O_2 pressure at the limit ($P_1(O_2)$) was 1.06 mmHg. Thus for example in the first experiment the initial oxygen pressure $P_0(O_2)$ was greater than $P_1(O_2)$ by 0.3 mmHg. This means that if the efficiency of the heterogeneous chain termination did not increase during the combustion, the self-acceleration of the process would stop after the combustion of this quantity of O_2 in excess over the limit. Since according to the stoichiometry of the process the decrease in the O_2 pressure, within an accuracy corresponding to the concentrations of the active intermediate chain-carrier species, is equal to the decrease in the pressure of the mixture as a whole ($\Delta P(O_2) = \Delta P$), then for a constant value of k_{het}^c the self-acceleration would stop (that is the kinetic curve would show an inflection) only at $\Delta P \cong 0.33$ mmHg. Fig.12 shows, however, that the self-acceleration stops well before this quantity of O_2 has undergone combustion. The inflection (see for example curve *1*) is observed at a value of ΔP equal to only 0.14 mmHg, that is at an O_2 pressure which is 18% greater than $P_1(O_2)$, measured in the same series of experiments. Fig.12 also shows that the combustion stops at $\Delta P = 0.29$ mmHg, that is at an O_2 pressure which is even slightly greater than $P_1(O_2)$. At the same time, if the efficiency of the heterogeneous chain termination were constant, then when this value of $P(O_2)$ had been reached, the reaction should have taken place at maximum rate. The same "premature" stoppage of the chain combustion also takes place in the second experiment.

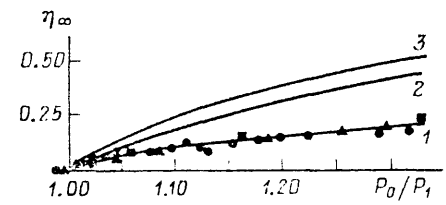

Figure 13. Dependence of the final degree of transformation of H_2 with O_2 on P_0/P_1: *1*) experiment over NaCl (the different point symbols correspond to the data from different series of experiments at 787 K); *2*, *3*) calculated from Eqn.(6) and from the analogous equation for the diffusion range.[95]

Fig.13 gives the dependence of the degree of transformation on P_0/P_1, obtained experimentally and calculated from Eqn.(6), and also using the analogous equation for the diffusion range of termination.[95] The results of the measurements are reproduced quantitatively in different series of experiments. The values of P_1 measured in different series also coincide. At the same time, the data show that the observed values of η_∞^{expt} are ~2.5 times lower than the results of the calculation which does not take account of the change in k_{het}^c during the combustion. The experimental values of the maximum rates are also several times smaller than the calculated values. Thus the results obtained show that self-retardation of the combustion of a $2H_2 + O_2$ mixture takes place over NaCl. This self-retardation is revealed primarily by the fact that the concentrations of the starting materials remaining after combustion are higher than the quantitatively reproducible limiting concentrations measured in the same experiments.

A noteworthy feature is that the first ignition limit of detonating gas in a quartz vessel with a non-continuous coating of MgO, for example, at 869 K is 3.88 mmHg, that is it is close to the value of P_1 over NaCl at 787 K. At the same time, in contrast to the combustion over NaCl, in the

case of MgO the values of w_{max}^{expt} and η_{∞}^{expt}, observed in the absence of self-heating, are appreciably greater than the calculated values obtained without allowance for the change in the properties of the surface during combustion.[19,62] The dependence on P_0/P_1 over MgO differs qualitatively from that observed over NaCl. The sorption of H_2O on NaCl is slight,[95] and, which is more important, does not lead to any significant increase in the specific rate of chain termination. Resonance fluorescence and emission spectroscopy have shown directly[97] that atomic hydrogen, formed in a flame of H_2 and O_2, with NaCl and KCl surfaces leads to the appearance of sodium and potassium atoms respectively in the gas phase. A change takes place in the chemical composition of the surface, which becomes darker. The reaction of the H atoms with the Cl^- ions of the crystal lattice apparently leads to the reduction of metal cations, some of which volatilise (metal atoms were detected in the gas phase), and some are oxidised. The heterogeneous destruction of atoms on the surfaces of metals and their oxides is extremely efficient.[6,50]

Reaction in the volume according to the scheme:

$$Na_2 + H \rightarrow Na + NaH$$

is also not excluded. In this case, the reproducibility of the kinetic data is ensured by the fact that the layer of NaCl above the quartz surface is sufficiently thick.

Analysis has shown[29] that self-retardation of the combustion of detonating gas also takes place in the experiments corresponding to the kinetic curves given in Ref.98; after combustion has stopped, the O_2 concentration remains higher than the concentration corresponding to the first ignition limit and measured in the same experiments. At the same time, if the rates of branching and termination are linearly dependent on the concentration of chain carriers, then it is known that the chain combustion undergoes self-acceleration until the concentration of the starting material is higher than the first ignition limit.[1-5] Thus if in Ref.98 the results of the measurements were reproduced, this means that in these experiments there was self-retardation of the combustion of H_2, which was not noted in the work cited. On the contrary, the authors cited,[98] pointing out the slight discrepancy between the experimental data and one of the approximate equations, and attributing this influence merely to the ballast volume, consequently point out the quantitative agreement between the experimental data on the dependence of the maximum rate on the decrease in pressure and the results of the calculation carried out using an equation which does not take account of the change in the state of the surface. This agreement was illustrated[98] using diagrams. The quantitative agreement between the calculation and the experimental data of Ref.98 was also mentioned in Refs.1 and 4. Since at the same time the kinetic curves giving the change in pressure in Ref.98, as already noted, show marked self-retardation of the combustion, good reproducibility apparently was not obtained. In Ref.99, in the section giving the data on the detection, above $K_2B_4O_7$, of "anomalously" high degrees of combustion of H_2, that is degrees of combustion greater than the calculated values, it is pointed out that in a vessel insufficiently pretreated by ignitions, the observed degrees of combustion are lower than the calculated values in the initial series of experiments.

Analysis of the regular features of the pulsed combustion of NCl_3 in various series of experiments in Ref.35 also reveal heterogeneous self-retardation of BCP over various surfaces.

In view of the non-uniformity of surfaces and the variety of heterogeneous processes, it is possible that in addition to reactions leading to the self-retardation of BCP, other process take place simultaneously on other centres, leading to a decrease in the efficiency of heterogeneous termination.

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In most experiments to reveal the heterogeneous factors and carry out the most complete investigation of their role in the mechanism of chain reactions (for example in Refs.2–4, 19–23, 25–29, and 32), the processes were carried out under isothermal conditions. At the same time it is obvious that the characteristic features of the chemical mechanism of BCP, including the change in the efficiency of heterogeneous chain termination, and also the reversible non-stationary nature of the properties of the surface, play an important part in the non-isothermal process (see Figs.5 and 8 and also Refs.19, 31, 61, and 64). Since heterogeneous termination is one of the principal routes for the removal of energy from the reaction system, the change in the rate "constant" of this termination influences the thermal conditions of BCP not only through the change in the kinetics of the combustion, but also directly.

It should be noted that the nature, rate, and role in the chain process of the reactions of sorbed chain carriers with molecular components differ fundamentally from the familiar heterogeneous decomposition of valence-saturated molecules, which is also sometimes accompanied by the removal of atoms and radicals into the reaction volume (see for example Refs. 12–14 and 100–107). The decomposition of the original molecules with the transfer of active fragments from the surface to the volume in the chain process is only heterogeneous chain initiation. A variation of this initiation is the decomposition of intermediate molecular products on the surface in many processes involved in the slow oxidation of organic compounds in the liquid and gas phases†.[47,75,101-103] Chain initiation by the reactions of molecular intermediate products (degenerate branching) increases the rate of the process. In the absence of appreciable self-heating, however, it cannot lead to the high rates characteristic of chain combustion or to "anomalous" features analogous to those described above.

The branching of the chains was not degenerate in any of the processes studied in a series of investigations to detect and study the non-stationary nature of the surface in chain combustion processes (see for example Refs.15, 19, 21, 22, and 32); in these processes, branching is brought about by active centres, that is free atoms and radicals, which undergo reactions differing qualitatively from decomposition. The lifetimes of these particles in the reaction mixture are much shorter than the time of the development of one chain. Thus the reaction chain during its development becomes branched, in contrast to the case of degenerate branching. The heterogeneous processes responsible for the observed regular features (for example in Refs.16, 19–23, 25–29, 32, 48, and 84) are also not due to the decomposition of intermediate species formed in the homogeneous stages. Moreover, the rates of the heterogeneous stages involving the chain carriers in the processes studied in the works cited are 10 times the rates of the reactions which play a role in degenerate-branched processes.

As noted in Ref.29, the reversible changes in the properties of the surface and the reactions of sorbed species should also have a significant influence in the combustion of hydrocarbons, including "cold flame" conditions and the

†In some liquid-phase oxidation processes, isomerisation of a peroxide radical takes place on the surface, with subsequent decomposition to a valence-saturated molecule and another radical.[102]

negative temperature dependence of the rate. Regular features indicating this type of heterogeneous process were observed in Refs.108–110, where it was shown that in the oxidation of hydrocarbons taking place only in the presence of a heterogeneous catalyst, the self-heating of the mixture in the centre of the reaction vessel is greater than that directly over the catalyst. The authors cited[108–110] also detected "hysteresis" phenomena, fluctuating hydrocarbon combustion conditions above the catalyst.

The emission of excited molecules from the surface into the gas phase, observed in some studies (see for example Ref.111) may also influence the kinetics of the chain reaction, if these molecules are involved in the stage limiting the rate of the process.

It was also pointed out in Ref.29 that the non-stationary nature of the properties of the surface should lead to a change with time in the rate "constant" of heterogeneous deactivation; in this process also, an inverse relationship to the state of the surface should be expected. This must be taken into account in processes taking place with the participation of excited species, including those in fluorination processes. Appreciable non-stationary character may also be shown by the value of the energy accommodation coefficient in heterogeneous recombination, both in chain processes and in plasma-chemical processes.

Thus a large number of new regular kinetic features have been detected for different types of BCP over different surfaces. The principal factors determining these regular features have been revealed. It has been shown that the development of chain combustion with time, and also the dependence of the main characteristics of the process on the initial conditions, differ qualitatively and quantitatively from those expected on the basis of earlier ideas which did not take account of the heterogeneous development of the chains and the reversible change in the efficiency of heterogeneous termination during combustion.

The above examples of the theoretical interpretation of the observed phenomena show that for the description of the regular kinetic features of BCP, the theory should take account of both those reactions whose rates are directly proportional to the concentrations of the chain carriers and those reactions whose rates show a non-linear dependence on these concentrations, while appreciable non-linearity appears in the course of the heterogeneous chain termination. Thus even in the initial stages of chain combustion, when the consumption of the starting materials can still be neglected, the process corresponds to non-linear differential equations.

The reversible changes detected and studied in the last twelve or thirteen years in the state, role, and composition of the solid surface during gas-phase branched-chain reactions, and also the marked influence of these changes on the process as a whole, are opening up new perspectives for the solution of various applied problems. Since heterogeneous recombination is accompanied by fairly strong chemisorption of chain carriers and their reaction with the solid surface, it is possible to bring about a directed change in the composition and properties of surfaces using appropriate chain processes (see for example Refs.22, 83, and 97). By selecting the solid material, it is possible to achieve the removal, from the surface into the gas reaction medium, of active intermediate species with the required chemical character, including species containing atoms from the solid phase.[97] By carrying out appropriate preliminary chemical modification of the surface using a gas-phase process, it is possible to bring about the chain reaction between the given starting materials for given initial conditions and ignition limits at different rates to give different final compositions (see for example Refs.19, 22, and 48).

The subsequent development of the theory of branched-chain processes and the solution of applied problems related to combustion or the existence of heterogeneous chain termination require allowance for the above regular features and factors.

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Radical Processes in the Adsorption of Olefins on Zeolites

A.A.Slinkin and A.V.Kucherov

The formation and reactions of radical species in the interaction of olefins with zeolites of different types are examined and the nature of the oxidation-reduction centres, the mechanism of the thermal reactions of radicals, and the possible role of radical structures in catalytic processes on zeolites are discussed.
The bibliography includes 37 references.

CONTENTS

I. Introduction 39
II. The formation of radicals in the adsorption of olefins on zeolites of the faujasite type 39
III. The nature of the radicals formed in the adsorption of olefins on mordenite 43
IV. The reactions of radical species at elevated temperatures on the HM zeolite and other zeolites 47
V. The influence of additives on the formation of radical species and their high-temperature reactions on the zeolite HM 49
VI. The formation and reactions of radicals on zeolites of the ZSM type 51

I. INTRODUCTION

The catalytic reactions and mechanisms of the adsorption of olefins on zeolites of different types have been the subject of numerous studies and their results have been surveyed in a number of monographs.[1-3] In the vast majority of the publications the catalytic and adsorption processes involving olefins are discussed taking into account the formation as intermediate species of carbonium ions or carbanions on Lewis or Brønsted centres.

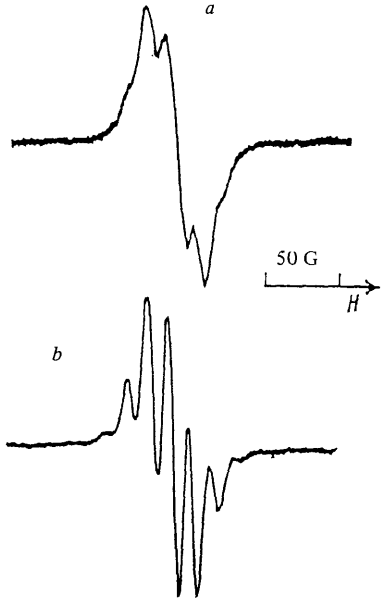


Figure 1. The EPR spectra arising in the adsorption of oct-1-ene (*a*) and pent-2-ene (*b*) from solution in CCl_4 on the lanthanide-form of the zeolite Y.[6]

Many fewer studies have been devoted to the radical species arising in the interaction of olefins with zeolites of different structure and to the nature of the centres initiating the formation of radicals, the mechanism of the thermal reactions of radicals, and their possible role in catalytic processes. This problem has acquired particular interest in recent years in connection with the discovery of the unique ability of high-silica zeolites to convert olefins into aromatic compounds.[4,5] The aim of the present review was to survey the available data concerning the mechanisms of the formation and reactions of radicals in the adsorption of olefins on zeolites and also to discuss the nature of the centres responsible for the one-electron charge transfer process.

II. THE FORMATION OF RADICALS IN THE ADSORPTION OF OLEFINS ON ZEOLITES OF THE FAUJASITE TYPE

The EPR spectra arising in the adsorption of olefins (2-methylbut-2-ene, 4-methylpent-2-ene, pent-2-ene, and oct-1-ene) on zeolites were apparently first published by Hirschler et al[6] (Fig.1): the adsorption was carried out from solutions in CCl_4 on the lanthanide-, Ca-, and Ce-forms of a type Y zeolite after their preliminary heat treatment at 500 °C in a stream of dry air. The same spectra, albeit slightly broadened owing to the high concentration of radicals, were observed in the adsorption of the pure olefins. The removal of the sorbed gases from CCl_4 (by evacuation) does not alter the EPR spectra, i.e. the oxygen contained in solution does not influence their characteristics.

The ratios of the intensities of the components of the spectrum (1 : 6 : 15 : 20 : 15 : 6 : 1) (Fig.1*b*) agree well with the EPR spectrum for the case of six equivalent protons with a hyperfine structure (HFS) constant a_H = 13.5 G. The EPR spectrum of oct-1-ene with the component intensity ratios 1 : 4 : 6 : 4 : 1 and a_H = 12.0 G corresponds to a species with four equivalent protons. The EPR spectra observed in the adsorption of 2-methylbut-2-ene and 4-methylpent-2-ene contain respectively 7 and 5 poorly resolved components with approximately binomial intensity ratios. The above values of a_H, which are approximately equal to half the corresponding values for the protons of the CH_3 group in the ethyl radicals (26.87 G), show, according to Hirschler et al,[6] that the unpaired electron in the radicals formed can be delocalised over two carbon atoms. It is fairly difficult to understand how radicals with five or six equivalent protons are formed from the adsorbed olefins mentioned above. It is believed[6] that the EPR signal produced can be associated with the olefin isomerisation or polymerisation products. At any rate, the polymer extracted from the zeolite, formed after the adsorption of pent-2-ene, gave rise to the

same EPR spectrum as that observed in the adsorption of pent-2-ene. Hirschler et al[6] do not express any views about either the nature of the centres on which the radical species are formed or the structure of the radicals formed.

Suzaki et al[7] continued the investigation of the properties of radicals arising in the adsorption of the olefin (but-1-ene) from the gas phase on the cation-substituted (Ce, Mg, Ca, Sr, Zn) zeolites Y and compared the rate of formation of the radicals with the rate of isomerisation of but-1-ene. The adsorption of but-1-ene on the CaY zeolite (degree of exchange 91.8%) at 25 °C leads to the appearance of a spectrum which is completely identical with that illustrated in Fig.1*b* with $a_H = 14.7$ G and $g = 2.002$. At temperatures from −16° to 25 °C and a but-1-ene pressure p ranging from 0.065 to 160 mmHg the steady-state concentration N of the radicals formed is expressed by the equation

$$N = N_s \frac{Kp}{1 + Kp}, \qquad (1)$$

where $N_S = 2 \times 10^{11}$ spins cm^{-2} and $K = K_0 \exp(\Delta H/RT) = 0.9$ (mmHg)$^{-1}$ (at $T = 25$ °C and for $\Delta H = 4.1$ kcal mole^{-1}); N_S amounts to 10^{-3} of the number of adsorbed but-1-ene molecules, i.e. 0.1% of the adsorbed olefin molecules are converted into radicals. A characteristic feature of the behaviour of the radicals formed is that they are stable if the gas phase contains but-1-ene molecules but recombine on evacuation (the EPR signal gradually disappears), the kinetics of this process being described by a second-order equation. If thermal desorption is carried out after the disappearance of the EPR signal, then it is possible to observe the presence of octane, octene, butane, butene, propene, and propane.

The experiments carried out by Suzaki et al[7] to investigate the influence of the zeolite dehydration temperature on the intensity of the EPR spectrum enabled them to put forward certain considerations about the mechanism of the formation of the radicals. Thus the possibility of the formation of a radical as a result of the transition of an H atom from the OH group of the zeolite to a but-1-ene molecule with formation of a 2-butyl radical is postulated†, because the intensity of the EPR spectrum increases by a factor of 15 on reducing the dehydration temperature from 600° to 250 °C. According to the authors,[7] the increase of the signal intensity after the addition of H_2O confirms the proposed mechanism and the formation of octane at temperatures above 100 °C and the decrease of the EPR signal intensity on evacuation are due to the recombination of the 2-butyl radicals. The seven equally spaced lines in the EPR spectrum have been explained by the interaction of the unpaired electron with the six equivalent hydrogen atoms of the radical formed. If this is true, then, as stated correctly by the above investigators,[7] the HFS constant should be the same as for the α- and β-protons in the butyl radical in the liquid phase, i.e. approximately twice as great as the measured value (14.7 G). The authors suggest that this contradiction cannot be eliminated by assuming the formation of the allyl radical as a result of the abstraction of a hydrogen atom from the but-1-ene molecule, because in this case it would be difficult to account for the influence of the dehydration temperature and the addition of H_2O on the EPR signal intensity.

Thus the authors[7] postulate the formation of the 2-butyl radical and suggest that the low HFS constant can be due either to the perturbation of the wave function of the unpaired electron under the influence of the electrostatic field of the zeolite lattice or to the decrease of the unpaired electron density of the carbon atom of the radical owing to the partial transfer of the electron to the zeolite, i.e. the formation of a partly charged 2-butyl radical.

Another important feature of the investigation of Suzaki et al[7] is the attempt to compare the concentration of radicals with the degree of isomerisation of but-1-ene and to show that the 2-butyl radical can behave as an intermediate in the isomerisation process. This idea is seemingly confirmed by four observations:

1. the number of radicals in different cation-substituted forms of the zeolite Y is correlated with the degree of conversion of but-1-ene (Table 1);
2. the dependence of the rate of isomerisation on the hydrocarbon pressure is of the same type as the corresponding dependence of the intensity of the EPR signal of the radical formed, which is described by Eqn.(1);
3. at a constant pressure the degree of isomerisation of but-1-ene changes following the addition of H_2O in proportion to the change in the EPR signal intensity; we may note that, when the EPR signal intensity changes by a factor of approximately 4, the degree of isomerisation is only slightly altered;
4. following the addition of O_2, the isomerisation reaction is suppressed and 2-butyl radicals are converted into peroxy-radicals.

Table 1. Dependence of the degree of conversion α of but-1-ene and the concentration of radicals N_S on the type of zeolite employed (β is the degree of exchange).[7]

Catalyst	β, %	$10^{-15} N_S$, spins/100 mg	α, %	Catalyst	β, %	$10^{-15} N_S$, spins/100 mg	α, %
CeY	91.8	200	88	ZnY	91.8	2	20
MgY	72.5	80	80	CuX	—	*	13
CeY	67.5	60	68	CoX	83.3	nil	5
CaY	93.2	10	58	MgX	96.8	nil	traces
CeX	—	10	37	ZnX	100	nil	traces
NH_4Y	90.5	9	72	TlX	100	nil	traces
SrY	97.6	4	65	NaY	100	nil	traces

*It may be that the EPR signal of the radical is not observed owing to its overlap by the signal due to the Cu^{2+} cation.

However, having measured the rate of isomerisation and the rate of formation of radicals using a mixture of deuteriated and non-deuteriated but-1-enes, the authors showed that the rate of isomerisation is higher, i.e. the 2-butyl radical is not an intermediate and is not in equilibrium with the intermediate of the isomerisation reaction. It is also assumed that a small proportion of 2-butyl radicals on the outer surface of the zeolite may be an intermediate product of the isomerisation process.

Although the authors[7] seemingly demonstrated that the radicals formed in the adsorption of but-1-ene on cation-substituted zeolites Y are not intermediates in the isomerisation reaction, this idea was again discussed by Otsuka et al.[8] They investigated the isomerisation of *cis*-but-2-ene at 25 °C on the zeolite HY (degree of exchange 86%) subjected to vacuum heat treatment in the range 400–650 °C. They studied the influence of promoting agents (CCl_4, $SiCl_4$, $GeCl_4$, $SnCl_4$, and HCl) on the rate of reaction and compared the latter with the concentration of the radicals formed on the initial and promoted zeolites. It was found that the rate of isomerisation on the zeolite evacuated at 650 °C increases sharply in the presence of preadsorbed CCl_4.

†Here and henceforth the radical $CH_3CH_2\dot{C}HCH_3$.

The promoting effect of CCl_4 is manifested only for zeolites heat-treated above 500 °C. An infrared spectroscopic study of the interaction of CCl_4 with the acid OH groups of the zeolite heat-treated at 650 °C showed that this interaction is weak and reversible: the entire adsorbed CCl_4 is removed by evacuation at room temperature.

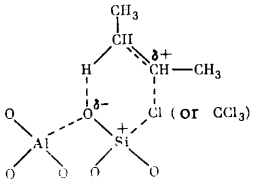
On the other hand, the data presented in Table 2 show that CCl_4 preadsorbed on the zeolite evacuated at 650 °C induces a sharp increase of the EPR signal intensity during the subsequent adsorption of *cis*-but-2-ene. The adsorption of the olefin on the clean specimen is accompanied by the appearance of only a weak EPR signal. It is noteworthy that this signal consists of a seven-component spectrum with $g = 2.003$ and $a_H = 14.5$ G and is almost identical with the signals observed by other workers;[6,7] among all the chloro-compounds investigated, only CCl_4 induces a sharp increase of the EPR signal intensity. The specimen evacuated at 400 °C is not subjected to the promoting effect of CCl_4 as regards the intensity of the EPR signal due to the adsorbed olefin and also the catalytic activity.

Table 2. The relative intensities I of the EPR signals of the radicals formed in the *cis*-but-2-ene + chloro-compound + zeolite HY system at 25 °C.[8]

Adsorbate	I, rel. units
CCl_4 + butene	17*
CCl_4 + butene	280
$SnCl_4$ + butene	21
$GeCl_4$ + butene	5
$SiCl_4$ + butene	13
HCl + butene	5
Butene	7
Butene	23**

*The temperature of the preliminary heat treatment of the zeolite was 400 °C; in the remaining cases it was 650 °C.
**After 24 h; in the remaining cases—after 1 h.

In conformity with the hypothesis put forward by Suzaki,[7] Otsuka et al. believe that the EPR spectrum observed during the adsorption of *cis*-but-2-ene is due to the formation of a partly charged 2-butyl radical, which is an intermediate in the isomerisation reaction, and the increase of the rate of the isomerisation reaction under the influence of CCl_4 is related to precisely this factor. The observed[8] increase of the rate of isomerisation under the influence of other chlorine-containing additives, which do not induce an increase of the EPR signal, has been explained by the modification of the Brønsted acid centres. The unique ability of precisely CCl_4 to promote the formation of radicals in the adsorption of the olefin is associated, according to Otsuka et al,[8] with the possibility of the dissociation of CCl_4 into the radical species CCl_3 and Cl (not detected by EPR) on centres arising in the high-temperature dehydroxylation. The CCl_3 or Cl radical species stabilised on the electron-accepting centre promote the formation of a partly charged 2-butyl radical on interaction of the olefin with the acid OH group. The proposed mechanism of the interaction is shown below:



The results of detailed studies of the interaction of various olefins with cation-substituted zeolites of the faujasite type have been described.[9–12] It is emphasised[9] that the adsorption of olefins on zeolites leads to the appearance of EPR spectra with an odd number of components, which cannot be explained, according to the author,[9] by the addition (or abstraction) of hydrogen atoms to (from) the olefin molecule, since the signal of such a radical would have had an even number of components (if all the hydrogen atoms in the molecule participate in the formation of the HFS). It is therefore suggested that the radical species arises as a result of electron transfer from the zeolite lattice to the olefin molecule. Data for the formation of the radical in the adsorption of but-1-ene on the zeolite CeX (68% exchange) are presented as an example. The EPR spectrum produced contains seven components ($g = 2.0037$, $a_H = 14$ G); the signal intensity is much greater in this case when the adsorption is carried out on a specimen activated *in vacuo* and then treated with O_2. It is suggested that an electron is transferred to the olefin molecule from the Ce^{3+} cation or from the reduction centre.

A further development of the study quoted above involved the investigation[10] of the formation of radicals in the adsorption of various olefins (propene, isobutene, *cis*- and *trans*-but-2-enes, but-1-ene, and *cis*- and *trans*-pent-2-enes). After the adsorption of the above olefins, EPR spectra containing seven and nine components and having a binomial distribution of intensity appear ($g = 2.0023 \pm 0.0005$, $a_H = 14$ G). The author[10] suggests that the radical species do not have the allyl structure, because 3,3,dimethyl-but-1-ene, which does not produce such a structure, gives rise to an identical EPR spectrum. Cyclic olefins (cyclopentene and cyclohexene) give rise to intense EPR signals with a poorly resolved HFS.

The following properties of the radical species may be noted in relation to the radicals formed in the adsorption of isobutene:

1. the radicals are stable at room temperature;
2. an increase of temperature to 50 °C entails an increase of signal intensity, which falls on further increase of temperature;
3. cooling to room temperature again results in the appearance of a signal with an HFS but with a lower intensity;
4. the radicals are stable when acted upon by O_2, CO_2, and H_2O: exposure of the specimens to air for several days does not result in the destruction of radicals;
5. the adsorption of H_2O, before the adsorption of the olefin or simultaneously with the latter, inhibits the formation of radicals.

The influence of various substituting cations in zeolites X and Y and also of the heat treatment conditions has been studied in greater detail by Krzyzanowski.[11] The appearance of a seven-component spectrum of the type described above in the adsorption of propene on zeolites X and Y containing the cerium, lanthanum, and praeseodymium cations proceeds, according to the author,[11] as a result of electron transfer from the lanthanide cation (particulary Ce^{3+}) to the propene molecule. The same mechanism of the formation of the radical has been put forward for the zeolite FeY containing Fe^{2+} cations capable of being converted into Fe^{3+}. However, zeolites containing Co^{2+} do not generate radicals following the adsorption of an olefin, like the zeolite CaX. The adsorption on the zeolite CaY results in the observation of a low-intensity EPR signal. The behaviour of zeolites AgY and AgX proved to be interesting.[11] In this case the EPR signal (an intense singlet with $g = 2.0025$ and a width $\Delta H = 7.2–7.4$ G) appeared also in the adsorption of ethylene, which had not been observed in studies involving other zeolites.

It is essential to note that for the zeolites CeX and CeY there exists a threshold degree of exchange which depends on the activation temperature and the type of zeolite and below which radicals are not formed in the adsorption of an olefin. Table 3 presents the corresponding data for the formation of radicals in the adsorption of but-1-ene. It is striking that the threshold concentration for the zeolite CeY is lower than for the zeolite CeX (particularly at low activation temperatures). This fact has been explained[11] by the lower degree of migration of cerium cations in the zeolite Y towards centres which are not readily accessible for interaction with olefinic centres (S_I in hexagonal prisms and $S_{I'}$ and $S_{II'}$ in sodalite cells).

Table 3. The influence of the degree of exchange β and the activation temperature T_a of the zeolites on their ability to form radicals.[11]

Type of zeolite	T_a, °C	β, %	n
CeX	300	40	11.3
CeX	450	45	12.7
CeX	550	56	15.8
CeY	300	15	2.8
CeY	450	20	3.7
CeY	550	55	10.3

Notation: n is the number of Ce^{3+} cations per unit cell.

The conditions of heat treatment and the atmosphere in which it is carried out exert a significant influence on the concentration of the radicals formed. For decationated zeolites and the zeolites CaY and CeY with degrees of exchange guaranteeing the localisation of the cations in the large cavities, an increase of the activation temperature from 200° to 600 °C is accompanied by an increase of the EPR signal intensity possibly as a result of the increase of the number of defects on dehydration. On the other hand, in the case of the zeolites CeX with large degrees of exchange, the activation temperature can promote the migration of the cations to inaccessible centres and can decrease the concentration of the radicals formed.

The activation of the zeolite in an O_2 atmosphere increases sharply the concentration of the radicals formed in the adsorption of an olefin[11] and the higher the activation temperature the greater the EPR signal intensity. The effect of activation increases both with increase in the degree of exchange and with increasing O_2 pressure at the given temperature. When the zeolites activated in O_2 are treated with hydrogen, the intensity of the EPR signal due to the radicals formed in the subsequent adsorption of olefins diminishes to a greater extent the higher the temperature of the treatment in H_2. For the cerium-containing zeolites, the activating influence of O_2 can be explained by the appearance of cerium cations in the highest valence states (for example, Ce^{4+}), which are involved in the one-electron transfer.

The influence of O_2 on the formation of radicals in the adsorption of butene on the zeolite CaNaX has been studied in greater detail by Krzyzanowski.[12] He was able to show that, when the treatment of the zeolite in O_2 at 200 °C is accompanied by the appearance of the O_2^- radical-anion, then the concentration of the latter diminishes in the adsorption of butene. It has been suggested that the butene molecule is converted into a radical by abstracting an electron from the oxygen radical-anion. Krzyzanowski[12] also observed the following extremely interesting effect: in the adsorption of butene on CeNaX the concentration of the O^- radical-anions initially rises sharply and then falls (Fig.2). This phenomenon was explained by the conversion of the diamagnetic forms of the oxygen anions (O^{2-} or O_2^{2-}) into the paramagnetic form O^- on interaction with butene molecule and by the subsequent decrease of the O^- concentration accompanied by the simultaneous increase of the concentration of organic radicals. Thus in the first instant of adsorption the olefin molecules behave as electron acceptors (the appearance of the paramagnetic form O^-) and are converted into radical-anions, after which the concentration of the O^- radical-anions diminishes either owing to the formation of the neutral form O and the subsequent increase of the concentration of the organic radical-anions or owing to the conversion of O^- into O^{2-}; in the latter case the olefin molecules behave as electron donors. Krzyzanowski[12] did not discuss the question which of these processes leads to a decrease of the O^- concentration.

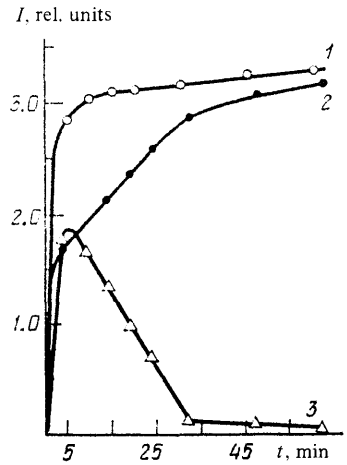


Figure 2. Variation of the intensity I of the EPR signals of radicals with the time t for the CeNaX-68 zeolite treated in N_2O at 500 °C (curves *1* and *3*) and 200 °C (curve *2*): *1*) and *2*) radicals formed in the adsorption of butene; *3*) O^- radical-ions.

Thus we have considered studies in which the formation of organic radicals was observed in the adsorption of olefins on decationated and various cationic forms of zeolites of the type of faujasite. Analysis of the results shows that at present there is not any single point of view both on the nature of the radicals formed and on the centres responsible for their appearance as well as their role in catalytic processes. We can only note the most important questions which have not yet been solved or which have received contradictory answers in studies by different investigators.

1. It has been shown that the adsorption of various olefins both from solution[6] and from the gas phase[7-12] on cationic and decationated forms of faujasites leads to the appearance of EPR signals which have virtually identical parameters. However, it is not clear whether this spectrum refers to a primary radical or an oligomeric radical or whether

it is characteristic of polymeric products which can be extracted from the zeolite surface.[6] It has been established that the heat treatment of the zeolite in O_2 increases significantly the intensity of the EPR signal during the subsequent adsorption of the olefin,[9,11,12] but data concerning the influence of O_2 and H_2O on the formation of radicals are contradictory. Thus it has been shown[6,10] that the presence of O_2 does not influence either the parameters of the EPR signal or its stability, while the adsorption of H_2O simultaneous with that of the olefin or its preliminary adsorption inhibits the formation of radicals. It has been established[7] that H_2O promotes the formation of radicals and that the form of the signal changes under the influence of O_2; this has been attributed to the formation of peroxy-radicals.

2. According to Suzaki et al.[7] and Otsuka et al.,[8] in the adsorption of olefins on faujasites alkyl radicals are formed as a result of the transfer of a hydrogen atom from the zeolite OH group to the olefin molecule and are stabilised by the partial transfer of electron density to the zeolite lattice. It is not clear whether this mechanism is sufficient for the stabilisation of the highly reactive alkyl radicals and, furthermore, on this assumption it is difficult to account for the strong activating influence of the treatment in O_2 and the appreciable increase of the EPR signal intensity on the cationic forms of zeolites (particularly the Ce-forms) compared with the H-form. The Ce^{3+} and Fe^{2+} cations cannot behave as radical-forming donor centres either,[9,11] because they are absent from the oxidised forms of zeolites. The Ce^{4+} cation functioning as an acceptor centre also cannot be regarded as responsible for the formation of radicals in the general case, because the latter are produced also on the decationated forms and on zeolites containing the Mg^{2+}, Ca^{2+}, and La^{3+} cations,[7] which do not behave as acceptor centres. The oxygen radical-anions formed under extremely specific conditions on the surfaces of faujasites[13] likewise cannot be regarded as the cause of the appearance of radicals in the adsorption of olefins, because in most cases they have not been detected either after the oxidative treatment of the zeolite or in the course of the adsorption of the olefin.

3. In our view, there is at present no convincing evidence that the above organic radicals are intermediates on faujasites, for example, in the isomerisation of olefins.[7,8] This hypothesis has been in essence rejected by Suzaki et al.,[7] although Otsuka et al.[8] later returned to it. Since the fraction of the radicals formed relative to the total number of adsorbed olefin molecules is 0.1%, it is evident that the amount of isomerisation products determined experimentally is due to the conversion of molecules which do not form radicals.

Next we shall consider the mechanisms of the formation and reactions of the radicals arising in the adsorption of olefins on high-silica zeolites, because in this case the available data permit a more detailed analysis of the nature of the radical-forming centres and of the structure of the radical species.

III. THE NATURE OF THE RADICALS FORMED IN THE ADSORPTION OF OLEFINS ON MORDENITE

The few studies devoted to the formation of radicals in the adsorption of olefins on mordenites dealt mainly with the character of the conformation and of the rotation of the radical species in the zeolite channels. Shih[14] obtained EPR spectra in the adsorption of *cis*- and *trans*-but-2-enes on the zeolite HM at low temperatures. It consists of a sextet of triplets arising owing to the interaction with the α- and β-hydrogen atoms, accompanied by the splittings a_{H_α} and a_{H_β} presented below:

Olefin	a_{H_β}, G	a_{H_α}, G	T, °C
cis-But-2-ene	16.2±0.4	8.2±0.4	−30
trans-But-2-ene	16.2±0.4	8.2±0.4	−50

Shih[14] assumes that the 16.2 G splitting is caused by the two identical CH_3 groups, while the 8.2 G splitting is due to the hydrogen atoms in the α-position, the small splitting by the α-hydrogen atoms being caused by the non-planar conformation of the alkene radical-cation.

The adsorption of tetramethylethylene on the zeolite HM at 25 °C is accompanied by the appearance of an EPR spectrum consisting of 13 equidistant components with a splitting of 17.5 G, corresponding to the interaction of the unpaired electron with the 12 equivalent protons.[15] The character of the spectrum changes little in the temperature range from −196° to 25 °C, which is due to the free rotation of the radical.

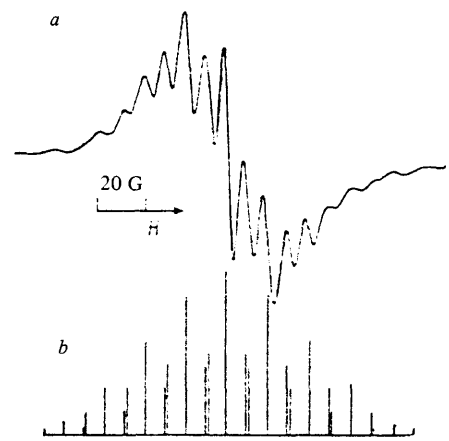


Figure 3. EPR spectrum arising in the adsorption of propene on the zeolite HM: *a*) experiment; *b*) calculation.

The EPR spectrum arising in the adsorption of a cyclic olefin (cyclopentene) on the zeolite HM was obtained in the same study.[15] A spectrum arises at −125 °C which can be accounted for by the splitting caused by the interaction with the four equivalent β-hydrogen atoms (a_{H_β} = 37 G) and two equivalent α-hydrogen atoms (a_{H_α} = 14.5 G). It is striking that in this case the splitting by the α-atoms is greater than in the case of the but-2-enes,[14] which is associated with the rigid planar conformation of cyclopentene. The observed EPR spectrum arising from the cyclopentene radical-cation[15] was accounted for on the hypothesis that the molecule rotates about an axis perpendicular to the five-membered ring. Calculation by the Hückel method showed that the unpaired electron is in a bonding π orbital and that its density is distributed equally between the two carbon atoms. Thus the splitting a_{H_α} = 14.5 G observed for cyclopentene is close to the value calculated from the McConnell relation $a_H = Q_{CH}\rho_C$ (Q_{CH} is a proportionality constant and ρ_C the π-electron spin density at the carbon atom), provided that Q_{CH} = 29.9 G (ρ_C = 0.5).

The adsorption of propene, but-1-ene, and pent-1-ene at 20 °C on the zeolite HM has been investigated by Leith.[16] All three hydrocarbons give rise to an EPR spectrum consisting of 19 lines with a_H = 8.1 G (Fig.3). The spectrum was described on the assumption that a radical of the type $CH_3-\overset{\beta}{C}H_2\overset{\alpha}{C}H=\overset{\alpha}{C}H=CHCH_3$ is formed from C_3H_6 and that the following interactions take place: (1) the interaction of one β-proton with one proton of the fixed CH_3 group (triplet with a_H = 33.6 G); (2) the interaction of one β-proton with two α-protons and with one proton of the CH_3 group (quintet with a_H = 16.8 G); (3) the interaction of the central proton with the last proton of the CH_3 group (triplet with a_H = 8.1 G). Heating to 100 °C reduces the splitting to 4.3 G and at 200 °C a broadened singlet with $\Delta H \cong 15$ G is observed. In our view Leith's description of the spectrum,[16] based on the concept of the formation of a linear dimer and of the presence of the three non-equivalent hydrogen atoms in one of the CH groups, is to some extent arbitrary. One should note that the observed spectrum is not sufficiently well resolved. However, Leith's observation[16] that the EPR spectra appearing in the adsorption of different linear olefins at 20 °C are identical is an important result.

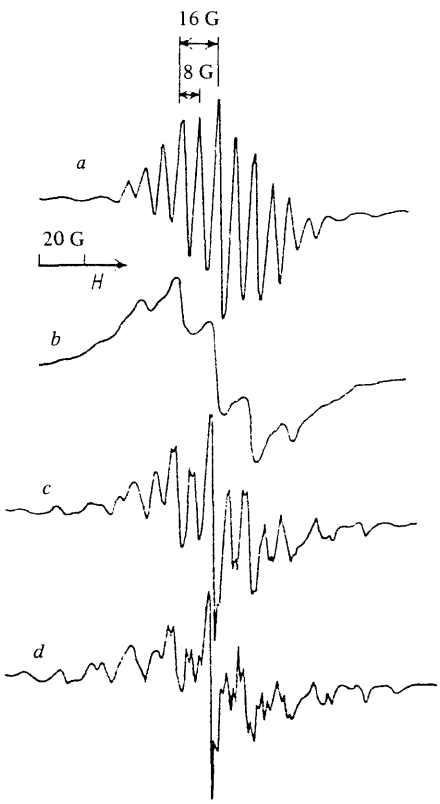


Figure 4. EPR spectra obtained 3 min (*a*), 1.5 h (*c*), and 8 h (*d*) after the adsorption of propene on the zeolite HM at 20 °C; *b*) spectrum of the specimen cooled to −196 °C after adsorption.

Unfortunately the studies of the formation of radicals in the sorption of olefins on zeolites HM examined above disregarded many important questions. (a) The nature of the primary radicals formed in the sorption of different olefins, the character of their thermal transformations, and the influence of various compounds on these processes were not analysed; (b) the structure of the centres responsible for the formation and reactions of the radical species was not discussed.

These problems were examined in greater detail in other investigations.[17-19] A study was made of the formation of radicals in the interaction of ethylene, propene, but-1-ene, isobutene, pent-1-ene, pent-2-ene, oct-1-ene, 2-methylhept-2-ene, cyclopentene, and cyclohexene with the zeolite HM. Fig.4 presents the EPR spectra observed in the adsorption of propene at 20 °C. Immediately after the adsorption of propene, an isotropic spectrum appears (Fig.4*a*); cooling the specimen to −196 °C is accompanied by the reversible conversion of this spectrum into that shown in Fig.4*b*. At 20 °C the spectrum in Fig.4*a* is slowly converted into that in Fig.4*c* (over a period of approximately 1.5 h) and further into the spectrum in Fig.4*d* (over a period of approximately 8 h). It is striking that the maximum intensity of the spectrum in Fig.4*a* is attained 5 min after adsorption, after which the signal intensity remains unaltered for approximately 6 h and corresponds to a spin concentration of 8×10^{17} spins g^{-1} (or one radical species per approximately 250 unit cells of the zeolite HM). Experiments involving the adsorption of propene on the deuteriated surface of the zeolite HM[17] showed that the hydrogen atoms of the radical species rapidly exchange with the OD groups of the zeolite HM even at −78 °C.

EPR spectra analogous to those illustrated in Fig.4 are observed in the adsorption of all the olefins investigated, except the cyclic olefins, at 20 °C. There are only some differences in the signal intensities and in the case of ethylene a spectrum with an HFS is observed against the background of a broader line.[20] These results confirm the data published earlier.[16]

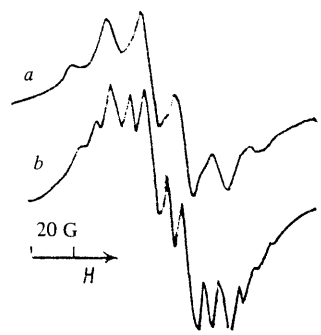


Figure 5. EPR spectra arising in the adsorption of propene on the zeolite HM at −78 °C: *a*) 2 h after adsorption; *b*) after brief warming of the specimen and recooling to −78 °C.

The identity of the EPR spectra obtained in the adsorption of various olefins shows that even at 20 °C rapid chemical reactions occur and the spectrum in Fig.4*a* is that of a radical with a secondary structure identical for different initial olefins. The data obtained in the study of the adsorption of olefins at a low temperature, where one can expect the formation of radicals from the unaltered molecules of the initial olefin, are therefore significant. For this purpose, a study was made[17] of the formation of radicals in the adsorption of ethylene, propene, but-1-ene, isobutene, pent-1-ene, and cyclopentene at −78 °C. It was noted that,

after the adsorption of ethylene on the zeolite HM at −78 °C, the EPR signal is not manifested for at least 3 h. The EPR spectrum arising in the adsorption of propene is illustrated in Fig.5*a*. Its intensity is appreciably lower than in the adsorption at 20 °C and its character remains unaltered for 5 h at −78 °C. A decrease of temperature to −196 °C is accompanied by an increase of the intensity of the broad line and the identical broadening of all the HFS components. A slow increase of temperature from −78 °C leads to an irreversible change in the EPR spectrum (Fig.5*b*), which is transformed at 20 °C into one of the type shown in Fig.4*a* and further into that in Fig.4*d*.

The adsorption of isobutene at −78 °C gives rise to the EPR spectrum shown in Fig.6*a*; cooling of the specimen to −196 °C results in the irreversible transition to the spectrum in Fig.6*b*. In this case too a gradual increase of the temperature of the specimen is accompanied by irreversible changes in the spectrum (Fig.6*c*). Fig.6*d* illustrates the spectrum obtained in the adsorption of but-1-ene at −78 °C; it coincides with that for the same olefin published by Shih.[14] The adsorption of pent-1-ene at −78 °C gives rise to the EPR spectrum of the type shown in Fig.4*a*, which is characteristic of the adsorption of propene at 20 °C. The changes in the spectrum on raising the temperature are identical with those shown in Figs.4*a*–4*d*.

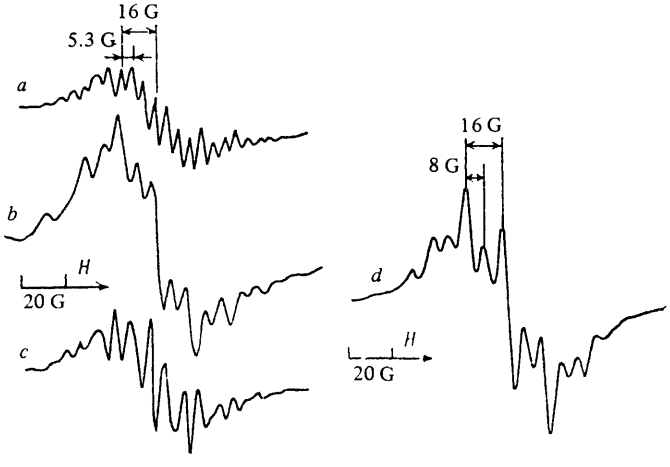


Figure 6. EPR spectra arising in the adsorption of isobutene (*a*–*c*) and but-1-ene (*d*) on the zeolite HM at −78 °C: *a*) 1 h after adsorption; *b*) after cooling to −196 °C; *c*) after brief reheating from −78 °C to 20 °C and recooling to −78 °C.

It is essential to note that the EPR spectra arising as a result of the interaction of all the olefins investigated with the zeolite HM[17] are stable only in the absence of oxygen; the introduction of O_2 at 20 °C leads to the instantaneous irreversible disappearance of the spectrum.

We shall analyse in greater detail the results of a study[17] of the first stage in the adsorption of olefins at 20 °C. The isotropic spectrum (Fig.4*a*), consisting of 11 equally spaced components with a splitting of approximately 8 G between them and non-binomial ratios of their intensities, is converted at −196 °C into the spectrum in Fig.4*b*, containing five equally spaced components with a splitting of 16 G and nearly binomial intensity ratios. Presumably, the radical species formed on adsorption contains two groups of protons: (1) a group of four equivalent protons (the interaction with these protons corresponds to a_H = 16 G), whose signal broadens slightly at −196 °C; (2) a group of two equivalent protons (giving a splitting of 8 G), whose signal broadens markedly at −196 °C. The EPR spectrum comprising eleven equidistant components, calculated on the basis of these postulates, has intensity ratios similar to those observed.

The fact that at 20 °C identical EPR spectra arise (Fig.4*a*) following the adsorption of different olefins, in which the number of substituents at the double bond varies from zero (ethylene) to three (2-methylhept-2-ene), can be explained by the formation of the same hydrocarbon radical fragment, which determines the structure of the EPR spectrum.

The set of data obtained for the adsorption of olefins at −78 °C confirm the hypothesis concerning the secondary nature of the radical giving rise to the spectrum of the type illustrated in Fig.4*a* and makes it possible to postulate the following reaction scheme and the following structure of the radical species. Evidently the EPR spectra arising in the course of the adsorption of olefins at −78 °C are due to the formation of primary radicals. The absence of the EPR signal in the adsorption of ethylene at this temperature shows that the radical-forming centre in the zeolite HM does not possess sufficient electron affinity to ionise the ethylene molecule, in view of its high ionisation potential compared with substituted olefins, and the appearance of an EPR spectrum of the type shown in Fig.4*a* when ethylene is adsorbed demonstrates ambiguously the occurrence of the oligomerisation reaction.

The EPR spectrum corresponding to the adsorption of propene at −78 °C (Fig.5*a*) indicates the formation under these conditions of a radical containing five equivalent protons. This radical, formed as a result of the abstraction of one hydrogen atom from the propene molecule, probably has an allyl structure in which all the hydrogen atoms are equivalent as a consequence of the delocalisation of the π-bond and rapid exchange. Although the hydrogen atoms in the free allyl radical are not equivalent,[21] the situation may be different for the species stabilised in the structure of the zeolite HM. As already stated above, heating of the specimen with propene adsorbed at −78 °C is accompanied by the disappearance of the spectrum shown in Fig.5*a* and the appearance of the spectrum of the type illustrated in Fig.4*a*. Formally these exchanges in the spectrum can be accounted for by the disappearance of one of the five equivalent hydrogen atoms, to which corresponds a_H = 16 G, and the appearance instead of a group of two hydrogen atoms (a_H = 8 G). From the standpoint of chemical reactions, such a change in the spectrum is probably associated with the alkylation of the allyl structure and the formation of a species in the spectrum for which a_H = 16 G is associated with the four α-protons of the allyl system and a_H = 8 G is associated with the two β-protons. The fact that the EPR spectrum of the radical formed in the adsorption of pent-1-ene at −78 °C is identical with that in Fig.4*a* apparently confirms the structure of the secondary radical species put forward above.

However, a different version of the structure cannot be ruled out either for the species giving rise to a spectrum of the type shown in Fig.4*a*, namely it can consist of an alkene radical arising without the elimination of a hydrogen atom, in the spectrum of which a_H = 8 G is due to the interaction with the two α-protons, while a_H = 16 G is due to the interaction with the four β-protons. The EPR spectra of the alkene radicals containing from four to six β-protons

differ little from one another and the distributions of the intensities of the eleven central components are similar in these three cases, while the components at the edges of the spectrum are weak.

We shall now consider the possible structure of the radicals formed in the adsorption of isobutene and but-1-ene at −78 °C. The EPR spectrum comprising 21 equidistant lines with a_H = 5.3 G (Fig.6*a*) can be interpreted if it is assumed that the adsorption of isobutene entails the formation of an alkene radical-cation in which six equivalent β-protons give rise to a septet with a_H = 16 G, while two α-protons give rise to a triplet with a_H = 5.3 G. The reduction of the temperature of the specimen to −196 °C inhibits the rotation of the radical, a_H for the α-protons increases to 8 G, and the spectrum of the type shown in Fig.6*a* degenerates into one of the type in Fig.6*b* (15 equidistant lines with a_H = 8 G). It should be noted that the spectrum of the type in Fig.6*a* cannot be accounted for by the formation of a radical species having the structure of an allyl type, i.e., in contrast to the adsorption of propene, the adsorption of isobutene involves the formation of an alkene radical-cation.

As stated above, the EPR spectrum arising in the adsorption of but-1-ene is identical with the spectra of sorbed *cis*- and *trans*-but-2-enes[14] and its HFS is due to a septet generated by the six β-protons and the triplet due to the two α-protons with a_H = 16.3 and 8.2 G respectively. It is of interest to note that the spectrum for but-1-ene (Fig.6*d*) is identical with that obtained in the adsorption of isobutene at −196 °C (Fig.6*b*), which indicates the presence in both radicals of six equivalent protons in two CH_3 groups and confirms the identical character of the radicals in these two cases.

In our view, the radical with the allyl structure is formed only in the adsorption of propene at −78 °C, while in the case of the remaining olefins the formation of radicals of the alkene type without the elimination of the hydrogen atom is probably preferred.

The set of data examined permits the conclusion that even at 20 °C, as a result of rapid reactions involving the isomerisation of the double bond, skeletal isomerisation, and oligomerisation, the primary radicals formed from different adsorbed olefins at −78 °C can give rise to oligomers of different structure and molecular weight containing a radical fragment having the same chemical structure and responsible for the appearance of identical EPR spectra. These structurally identical radical fragments are localised in sections of the mordenite lattice with a specific geometry and this constitutes the manifestation of the unusual "matrix" effect of the zeolite.

We shall attempt to carry out an analysis in order to discover the process with which the slow changes in the structure of the EPR spectra at 20 °C can be associated (Figs.4*a*, 4*c*, and 4*d*). Data for the adsorption of C_3D_6 at 20 °C show that the integral intensity of the EPR signal does not change over several hours, i.e. the changes in the HFS if the spectrum are not associated with the change in the concentration of the radical species. Analysis of the HFS of the spectra in Figs.4*c* and 4*d* suggests that they are anisotropic, i.e. the changes in them are not related to a change in the structure of the radical fragments formed. In this case the gradual transition from the isotropic (Fig.4*a*) spectrum to the anisotropic (Figs.4*c* and 4*d*) spectra can be caused by the transition from the initial disordered disposition of the radical species to an ordered arrangement of the latter in space in the geometrically regular mordenite structure. The ordering process is accompanied by the inhibition of the rotation of the radical species, which is demonstrated by the fact that, on cooling to −196 °C, the isotropic spectrum (Fig.4*a*) changes its shape markedly (Fig.4*b*), while the spectrum in Fig.4*d* hardly changes on cooling in this way. Thus presumably at 20 °C there is rapid initial formation of radical fragments, which are gradually accommodated in lattice elements with a specific geometry, distributed regularly in the mordenite structure, and produce a "sublattice" of ordered radicals.

For the adsorption of C_3H_6 on the zeolite HM at 20 °C, Leith[16] recorded an EPR spectrum identical with that shown in Fig.4*c* but less well resolved, i.e. it can be regarded as an intermediate form of a slowly changing signal.

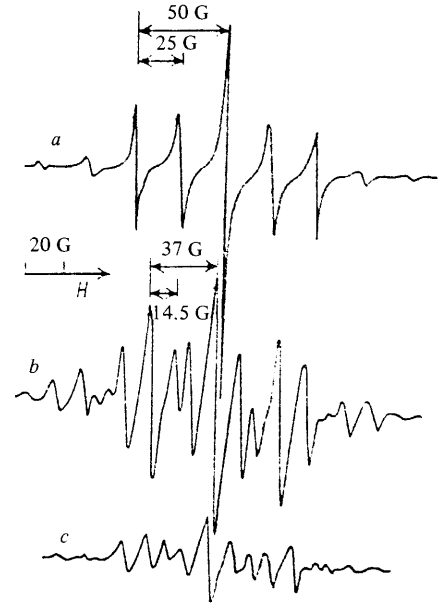


Figure 7. EPR spectra observed in the adsorption of cyclopentene on the zeolite HM: *a*) 3 min after adsorption at −78 °C; *b*) after cooling to −196 °C; *c*) at 20 °C.

Kucherov and Slinkin[17] also described unusual changes in the structure of the EPR spectra of cyclic olefins (cyclopentene and cyclohexene) as the temperature is altered. Fig.7 presents the EPR spectra arising in the adsorption of cyclopentene on the zeolite HM. Its adsorption at −78 °C is accompanied by the rapid appearance of the spectrum in Fig.7*a*, which does not vary with time. Cooling of the specimen to −196 °C leads to the reversible conversion of the signal into the spectrum shown in Fig.7*b*. An increase of the specimen temperature to 20 °C is accompanied by the irreversible transition from the spectrum in Fig.7*a* to that in Fig.7*c*, which then remains unaltered at 20 °C for at least 18 h. It is significant that the disappearance of the signal due to the adsorbed cyclopentene radical-cation on treatment with O_2 is reversible; in contrast to the radical-cations of olefins, the spectrum in Fig.7*c* is fully restored on evacuation of the system for 2–4 h at 20 °C.

The results were accounted for by Kucherov and Slinkin[17] in the following way. The nine line spectrum (Fig.7*a*) with non-binomial intensity ratios, arising in the adsorption of cyclopentene at −78 °C, is due to the formation of an alkene radical species in which there are two groups of protons: two equivalent α-protons (to which corresponds a_H = 50 G) and four equivalent β-protons (a_H = 5 G). The spectrum

in Fig.7*b* agrees well with that obtained earlier[15] for the adsorption of cyclopentene on the zeolite HM at −125 °C. This spectrum is due to an alkene radical and consists of 15 HFS components; it is possible to identify in this spectrum a quintet (a_H = 37 G) due to four β-protons and a triplet (a_H = 14.5 G) due to two α-protons. The spectrum in Fig.7*c* arising at 20 °C has an HFS which differs little from that of the spectrum in Fig.7*b*; consequently, at temperatures ranging from −196 °C to 20 °C, the chemical structure of the cyclic alkene radical-cation remains unaltered and only the degree of freedom of its rotation changes.

In order to understand the mechanism of the reactions of olefins on high-silica zeolites, it is extremely important to examine the character of the thermal transformations of the radical species formed following the adsorption of various olefins on the zeolite HM; the existing information about these reactions is discussed in the next Section.

IV. THE REACTIONS OF RADICAL SPECIES AT ELEVATED TEMPERATURES ON THE HM ZEOLITE AND OTHER ZEOLITES

The reactions of C_2–C_8 olefins, cyclopentene, cyclohexene, and also a series of compounds having a significantly different chemical structure, namely acetylene, butadiene, allyl chloride, allyl alcohol, n-hexane, cyclohexane, and methyl alcohol, have been investigated[18] on the H-forms of zeolites whose characteristics are given below:

Zeolite	SiO_2/Al_2O_3	Degree of decationation, %
HM	10	92
HM-26	26	99
HY	4.3	70
HKL	5.2	82
H-Cesite	5.2	95

The EPR spectra observed on heating an HM zeolite specimen with propene adsorbed at 20 °C are illustrated in Fig.8. The changes in the HFS shown in Fig.8 are typical for all C_2–C_8 olefins. We may note that the introduction of O_2 leads to the immediate disappearance of the spectra in Figs. 8*a*–8*c*, while the spectrum in Fig.8*d* not only does not disappear in the presence of oxygen but its intensity actually increases markedly with retention of the HFS. In the adsorption of olefins on the HM zeolite specimen heated to 300 °C the spectrum shown in Fig.8*d* appears immediately. The adsorption of olefins in air is not accompanied by the appearance of an EPR signal, but the subsequent heat treatment of the system in the presence of O_2 at 250–300 °C leads to the appearance of an intense signal of the type illustrated in Fig.8*d*. The same EPR signal appears on heating the zeolite HM with adsorbed cyclopentene and cyclohexene at 300 °C.

The adsorption of acetylene and allyl chloride on the zeolite HM at 20 °C with subsequent heat treatment at 300 °C likewise leads to the appearance of the spectrum shown in Fig.8*d*. An analogous process proceeds also when butadiene and allyl alcohol are adsorbed on the zeolite HM with subsequent heat treatment at 300 °C. It is remarkable that the EPR spectrum of the type in Fig.8*d* arises also on heating the HM zeolite specimen at 250–300 °C with saturated compounds such an n-hexane, cyclohexane, and methanol.

Thus, for all the compounds enumerated above adsorbed on the zeolite HM, heat treatment at 250–300 °C leads to the appearance of the same EPR spectrum of the type shown in Fig.8*d*: the HFS of the EPR spectra arising in the reactions of different compounds are identical and there are only insignificant differences in the resolution of the individual components.[18]

In order to understand the nature of the signal generated, a study was made of the interaction of benzene and toluene with the zeolite HM at 300 °C. In both cases intense symmetrical singlets with ΔH = 3.7 and 7 G respectively arise at this temperature.

Apart from the zeolite HM, the EPR spectra generated in the high-temperature (up to 450 °C) interaction of benzene, n-hexane, and methanol with the zeolites HY, HKL, and H-cesite have been investigated.[18] In contrast to the zeolite HM, heating of all the zeolites investigated up to high temperature produces singlet EPR spectra without any HFS. Only on mordenite with a higher modulus (the zeolite HM-26 was obtained by direct synthesis) do n-hexane and methanol give rise on heat treatment to 350 °C to the EPR spectrum of the type shown in Fig.8*d* having a somewhat poor resolution of the HFS components compared with the zeolite HM.

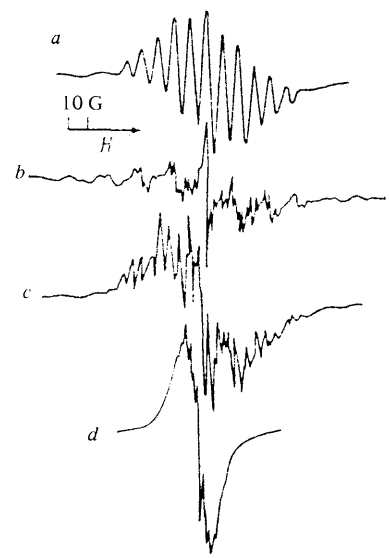


Figure 8. EPR spectra arising on heating the zeolite HM specimen containing propene adsorbed at 20 °C: *a*) at 20 °C, 5 min; *b*) at 90 °C, 50 min; *c*) at 200 °C, 15 min; *d*) at 300 °C, 20 min.

Thus only the zeolite HM possesses the unique ability to generate selectively, after the adsorption of compounds of different classes (unsaturated and saturated) at 250–300 °C, a structure giving rise to a characteristic EPR spectrum. We shall consider the nature of the radical generating this type of EPR spectrum.

It has been shown[17] that, when olefins of different types are adsorbed on the zeolite HM at 20 °C, the same radical fragment is formed rapidly and then undergoes further transformations on raising the temperature. The disappearance of the EPR signal produced on heating the specimen to 200 °C, after the addition of O_2, is probably associated with the retention by the radical formed of an alkene (or allyl) structure. However, the appearance at 250–300 °C of radical species resistant to the action of O_2 (the spectrum in Fig.8*d*) suggests that their chemical nature has changed fundamentally. It is known that radicals formed in the adsorption of aromatic compounds on zeolites are resistant

to the action of O_2.[22] In an earlier study[16] it was already suggested that the high-temperature treatment of propene adsorbed on the zeolite HM is accompanied by the formation of radicals of this kind. It has been shown[18] that, after adsorption with subsequent high-temperature treatment of all the zeolites investigated, benzene and toluene produce a singlet EPR spectrum. The EPR spectra obtained in the adsorption of isomeric xylenes on the zeolite HM at 20 °C have also been published;[18] the fact that the EPR spectrum appearing after the adsorption of *o*-xylene is identical with the spectrum Fig.8*d* arising on heat treatment of zeolite HM specimens with various compounds adsorbed on them is noteworthy. It is striking that the EPR spectrum arising following the adsorption of *o*-xylene is extremely stable at temperatures up to 300 °C in an oxidising atmosphere and fully retains its HFS. The EPR spectra for *m*- and *p*-xylenes adsorbed on the zeolite HM are converted into a spectrum of the type shown in Fig.8*d* on heating to 200 °C.

Thus it can be seen that the adsorption of compounds of different classes on the zeolite HM at 250–300 °C produces selectively adsorbed 1,2-dialkylphenylene radicals. We use by convention the term 1,2-dialkylphenylene radicals for the radicals giving a spectrum of the type in Fig.8*d*, because they are spectroscopically identical with the radicals formed in the adsorption of *o*-xylene, whose EPR spectrum does not change on raising the temperature from 20° to 300 °C. It is noteworthy that the EPR spectrum in Fig.8*d* with equally spaced components and $a_H = 1.8$ G cannot be described using the known HFS constants for the protons of the benzene ring and the CH_3 groups of the *o*-xylene radical-anions.[23] This may be caused by a change in the chemical composition of the adsorbed radical compared with the *o*-xylene molecule or by a change in the HFS constants of the hydrogen atoms for the adsorbed radical compared with the radical in the liquid phase.

The following questions arise in the analysis of the results:

1. what can be the general chemical mechanism of the reactions leading to the formation of aromatic molecules from compounds of different classes on the zeolite HM;
2. what can be the causes of the selective formation of adsorbed radicals with a specific structure on the zeolite HM at high temperatures.

The mechanism of the chemical reactions leading to the formation of aromatic compounds on the H-forms of high-silica zeolites from unsaturated and saturated hydrocarbons is still not known. It is only clear that it must be complex because hydrogenation–dehydrogenation reactions do not take place on these zeolites. Presumably the process proceeds via the complex disproportionation of the initial molecules with formation, on the one hand, of light saturated compounds and, on the other, of unsaturated compounds. As a result, a non-cyclic hydrocarbon fragment with a high degree of unsaturation, for example, tetraene, whose cyclisation leads to the formation of an alkylated aromatic compound, may be formed on the active centre on the zeolite surface. Aromatic molecules may be formed in this way not only from unsaturated but also from a series of saturated compounds, which are initially converted into olefins by the abstraction (in the form of CH_4) of the terminal group.

This idea about the character of the process agrees with the conclusions of a study[24] of the synthesis of compounds on the zeolite HM from labelled [2-^{13}C]isobutene and it has been suggested that aromatic molecules are formed via intermediate dimerisation and triene formation stages. Analysis of the reactions of n-hexane, cyclohexane, and cyclohexene when these are adsorbed on the zeolite HM also shows that the cracking and oligomerisation reactions play a decisive role in high-temperature transformations. The formation of benzene, whose heat treatment would yield products characterised by a narrow singlet ($\Delta H = 3.7$ G) in the EPR spectrum, might have been expected for the above compounds, particularly cyclohexene. However, experiments showed that these compounds form 1,2-dialkylphenylene radicals, which indicates a complex mechanism for the formation of the aromatic ring. For example, the process involving cyclohexane should proceed via ring opening with formation of an olefin and its oligomerisation followed by cracking with formation of polyenes and their ring closure to give the aromatic system.

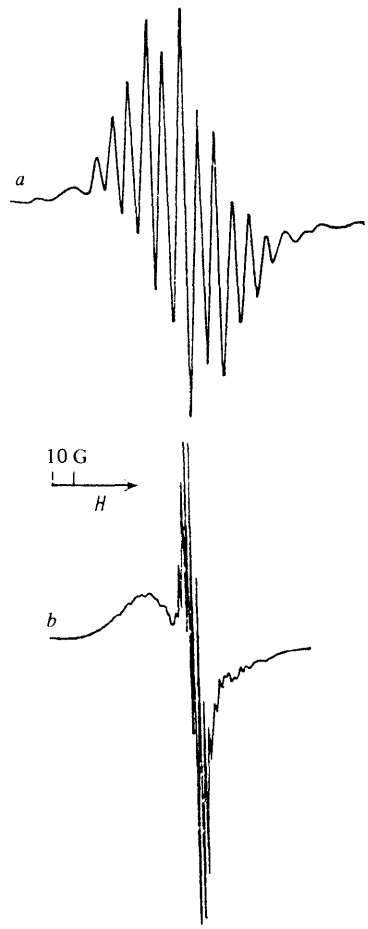


Figure 9. EPR spectra observed in the successive interaction of propene, benzene, and oxygen with the zeolite HM at 20 °C: *a*) zeolite HM + C_3H_6; *b*) (zeolite HM + C_3H_6) + C_6H_6 + O_2.

The data available do not yet permit the final conclusion that the formation of aromatic compounds from various starting materials on high-silica zeolites is a radical process, but one cannot rule out that the intermediate radical species are important participants in this process.

The understanding of the nature of the centres propagating the formation of aromatic compounds on high-silica zeolites is extremely important for the elucidation of its mechanism. An attempt to solve this problem has been undertaken.[19]

V. THE INFLUENCE OF ADDITIVES ON THE FORMATION OF RADICAL SPECIES AND THEIR HIGH-TEMPERATURE REACTIONS ON THE ZEOLITE HM

Initially we shall consider the experimental results obtained in a study[19] of the influence of added O_2, NH_3, H_2O, and SO_2 on the adsorption of an olefin (C_3H_6) and an aromatic compound (C_6H_6) on the zeolite HM.

Fig.9 presents the EPR spectra arising on consecutive interaction of C_3H_6, C_6H_6, and O_2 with the zeolite HM at 20 °C. The adsorption of C_3H_6 leads to the appearance of the 11-component signal described above. After the evacuation of the gas phase and the adsorption of C_6H_6, a signal due to the benzene-radical cation is not observed. Subsequent admission of O_2 leads to the immediate disappearance of the signal shown in Fig.9*a* and the appearance of the characteristic intense seven-component signal (Fig.9*b*) due to the benzene-radical cation.

Data[19] concerning the influence of the preliminary adsorption of NH_3 and H_2O on the concentration of the radical species formed in the interaction of C_3H_6 and C_6H_6 with the zeolite HM at 20 °C are presented in Fig.10. Evidently the adsorption of NH_3 and H_2O induces only a decrease of the intensity of the EPR signals but does not affect the HFS of the spectra arising following the adsorption of C_3H_6 and C_6H_6, i.e. it affects the amount but not the structure of the radical species; both NH_3 and H_2O inhibit the formation of radical-cations from C_6H_6 molecules at 20 °C to a much greater extent than the formation of radical species from C_3H_6.

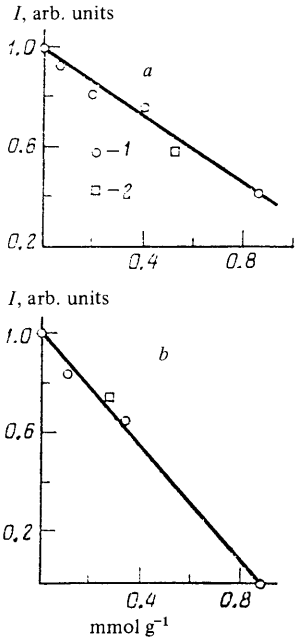


Figure 10. Dependence of the intensity I of the EPR signals in the adsorption of C_3H_6 (*a*) and C_6H_6 (*b*) at 20 °C on the amounts of NH_3 (1) and H_2O (*2*) preadsorbed on the zeolite HM

It is essential to note that at 20 °C the inhibiting effect of H_2O molecules described above is analogous to the effect of NH_3, while in the high-temperature (300 °C) heat treatment of the zeolite HM containing the chemisorbed C_3H_6 the adsorbed H_2O molecules do not prevent the formation of 1,2-dialkylphenylene radicals, while NH_3 molecules exert a powerful inhibiting effect on the process: the adsorption of 0.86 mmole of NH_3 per gramme of the zeolite HM fully suppresses the formation of 1,2-dialkylphenylene radicals.

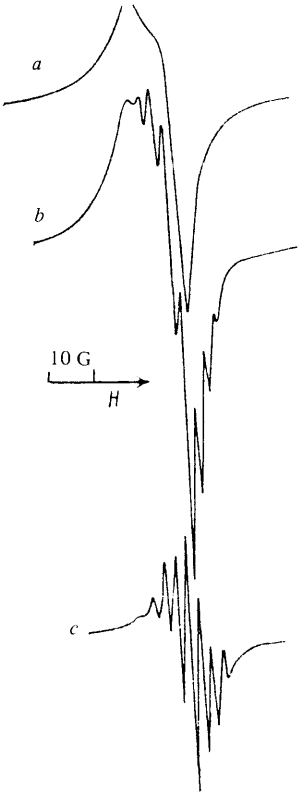


Figure 11. EPR spectra observed on interaction of the zeolite HM with SO_2 and C_6H_6 at 20 °C: *a*) zeolite HM + SO_2; *b*) (zeolite HM + SO_2) + C_6H_6; *c*) after the admission of air.

Fig.11 presents the EPR spectra[19] arising on successive interaction of SO_2 and C_6H_6 with the zeolite HM at 20 °C. The adsorption of SO_2 on the evacuated zeolite HM specimen is accompanied by the appearance of a signal (Fig.11*a*) analogous to that described by Ono and co-workers[25,26] and interpreted by them as a signal of the SO_2^- radical-anion. The adsorption of C_6H_6 on the zeolite HM specimen containing preadsorbed SO_2 is accompanied by a very rapid transition from the spectrum shown in Fig.11*a* to that in Fig.11*b*, which consists of a superposition of the spectrum in Fig.11*a* due to the SO_2^- radical-anion with unaltered intensity and the seven-component signal of the benzene radical-cation. The subsequent adsorption of O_2 leads to a transformation of the spectrum in Fig.11*b* into that in Fig.11*c*, i.e. to a marked decrease of the intensity of the signal of SO_2^- for a constant intensity of the spectrum of $C_6H_6^+$.

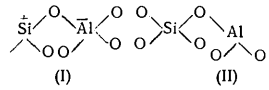
A completely different pattern arises in the successive interaction of the zeolite HM with SO_2 and C_3H_6 at 20 °C. In this case the adsorption of C_3H_6 induces a sharp increase of the intensity of the signal of the SO_2^- radical-anion (by a

factor of approximately 5) and the intensity of the 11-component spectrum is much smaller than in the interaction of the zeolite HM with C_3H_6 in the absence of SO_2.

Finally, in contrast to NH_3, the adsorption of SO_2 does not influence the formation of 1,2-dialkylphenylene radicals in the high-temperature reaction of adsorbed hydrocarbons.[19]

In order to understand the chemical nature of the centres on which the olefin and aromatic radicals are formed, it is necessary to concentrate attention in the first place on the characteristic features of the influence of O_2 on the formation of radicals from olefins and aromatic compounds. The following facts should be noted: (1) for the formation of radical-cations, it is essential that the oxidative centre in the zeolite HM should be activated by the chemisorbed O_2;[22] the presence of O_2 in the gas phase does not interfere with the formation of aromatic radical-cations and does not influence the HFS of the EPR spectra; (2) the formation of radicals from olefins hardly requires the activation of the oxidative centres on the zeolite HM surface by oxygen and the presence of O_2 in the gas phase leads to the irreversible destruction of these radicals.

It might have been supposed that radicals are formed from olefins and aromatic compounds during adsorption on two different types of oxidative centres, some of which are not activated, while others are activated by O_2, i.e. these centres can have different chemical structures. In a study of zeolites of the type of faujasite[27] it was observed that their dehydroxylation can produce Lewis centres of two types#:



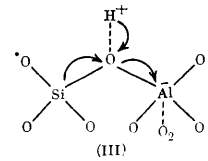
(I) (II)

We shall assume that the centres (I) and (II) are equally accessible to olefin (C_3H_6) molecules and the molecules of the aromatic hydrocarbons (C_6H_6), the aromatic molecule being adsorbed more strongly on the activated centre than the olefin molecule. Aromatic and olefin molecules are then formed respectively on the centres (I) and (II). If this were so, then, under the conditions of the experiment (Fig.9) on the successive interaction of C_3H_6, C_6H_6, and O_2 with the zeolite HM, the adsorption of C_3H_6 on the zeolite would have led to the formation of olefin radicals both on the centres (I) and (II), while in the successive adsorption of C_6H_6 its molecules would have displaced the olefin radicals from the centres (I). As a result the intensity of the EPR signal should diminish, but this effect has not been observed. It is difficult to suppose that the preservation of the intensity of the EPR signal due to the olefin radicals after the adsorption of C_6H_6 is due to the inaccessibility of the centres (I) to benzene molecules. It is more logical to assume that the olefin and aromatic radicals are formed on oxidative centres of the same type.

Before considering the nature of this centre, we shall note that it must differ from the structure of the centres (I) and (II) postulated for faujasites, because radical-cations are not formed on the zeolite HY after the adsorption of C_6H_6, while the adsorption of C_3H_6 results in the formation of a radical resistant to the action of O_2 and giving rise to a very weak five-component spectrum and a binomial distribution of intensities.[6-8] In addition it is significant that heating of the zeolite HM specimen to 450 °C is not accompanied at all by the formation of Lewis centres of types (I) and (II).[28]

The centre (II) is more characteristic of mordenite rather than zeolites of the type of faujasite.

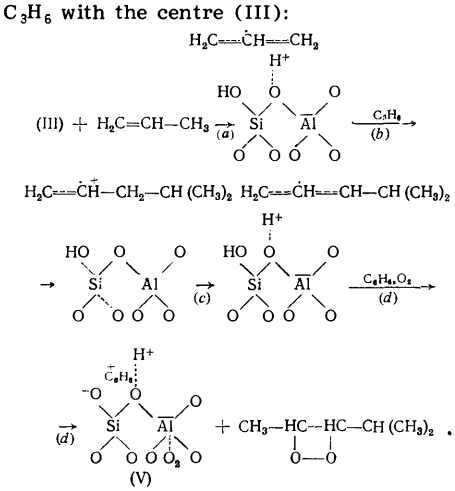
Thus it is necessary to assume the existence in the zeolite HM of active centres of a fundamentally different kind, arising at low heat-treatment temperatures (200–450 °C). In analysing the nature of the oxidative centre in the zeolite HM, the authors[19] considered the following structure:



(III)

It has a Brønsted centre, a radical acceptor centre, and an O_2 molecule chemisorbed on Al, which plays the role of an activator in the formation of aromatic radical-cations.

The possibility of the existence in SiO_2 of Si–O· and Si· centres and their reactivity has been investigated.[30-32] It is possible to imagine the following mechanism of the interaction of C_3H_6 with the centre (III):



An allyl radical is formed in stage (*a*) with transfer of a hydrogen atom to the radical centre, while in stages (*b*) and (*c*) dimerisation with participation of the bridging proton takes place. After the adsorption of benzene and the subsequent adsorption of O_2, the allyl radical is oxidised and destroyed [in stage (*d*)] and the benzene radical-cation is formed. It should be noted that dimerisation can precede the formation of the radical and in the case of C_2H_4 the process should proceed precisely in this sequence. It is significant that the interaction of the centre (III) with C_3H_6 is accompanied not only by the formation of an allyl radical but also probably by the removal of the activating oxygen, because otherwise the adsorption of C_6H_6 in stage (4, *d*) might have led to the formation of benzene radical-cations without the additional introduction of O_2 into the system. In the adsorption of C_6H_6 on the zeolite HM specimen containing adsorbed olefin radicals the C_6H_6 molecules are apparently localised within the zeolite channels near the centre (IV) and after the introduction of O_2 into the system are rapidly converted into radical-cations with formation of the centre (V).

The data for the inhibiting effect of NH_3 and H_2O on the formation of radicals from C_3H_6 and C_6H_6 (Fig.10) indicate a complex structure of the oxidative centre and can be readily understood if it is supposed that the centre has the structure (III). The adsorbed NH_3 molecule interacts with the bridging H^+ ion of the centre (III), which prevents the formation of an oligomeric radical [stage (*b*)]. Comparison of the data obtained with the results described by the present authors[17,18] permits a somewhat more detailed specification of the scheme presented above. Monomeric allyl

radicals [stage (*a*)] are formed in a small amount in the adsorption of C_3H_6 on the centres (III) at −78 °C. Heating of the system to 20 °C is accompanied by a sharp increase of the intensity of the EPR spectrum and a change of its HFS owing to the formation of oligomeric radicals.[17] An increase of the concentration of the radical species as a result of oligomerisation and a decrease of the ionisation potential (for example, from 9.94 eV for C_3H_6 to 8.9 eV for 3-methylbut-2-ene) makes it necessary to postulate the inhomogeneity of the centres (III) of the zeolite HM in terms of their oxidising power.

We may note that the oligomerisation process need not necessarily be associated with participation of the most acid protons. When only the strongest Brønsted centres are involved in oligomerisation, the EPR spectrum would cease to be observed after the adsorption of only approximately 0.35 mmole of NH_3 per gramme of the zeolite HM (centres for which the heat of adsorption of NH_3 is 140 kJ mol^{-1}).[33] Thus the combination of the strongest oxidising and acid properties is not obligatory for the centre (III).

The adsorption of NH_3 prevents not only the formation of radicals from the adsorbed olefin at 20 °C but also the high-temperature aromatisation of various compounds with formation of 1,2-dialkylphenylene radicals,[18] which is due to the strong interaction of the NH_3 molecules with centres of type (III) on the zeolite HM.

The mechanism of the decrease of the intensity of the EPR signal of the benzene radical-cation on adsorption of NH_3 (Fig.10*b*) is less clear, because in this case the H^+ ion is not involved directly in the formation of the radical although it can interact with the aromatic ring, causing its partial polarisation. It is significant that the decrease in the concentration of the benzene radical-cations under the influence of the adsorption of NH_3 is accompanied also by a decrease in the intensity of the singlet EPR signal arising on heating the specimens to 150–300 °C.

The adsorption of H_2O, like that of NH_3, inhibits the formation of radicals both in the adsorption of C_3H_6 and in that of C_6H_6, apparently as a result of the analogous blocking of the centre (III). It is striking that, in contrast to NH_3, H_2O is desorbed on raising the temperature and does not prevent the conversion of the adsorbed C_3H_6 into 1,2-dialkylphenylene radicals.

We shall now discuss the influence of the addition of SO_2 on the formation of radicals in the adsorption of an olefin and the aromatic compound. There are significant differences in the influence of adsorbed SO_2 on the concentrations of these radicals. On the one hand, the intensity of the EPR signal of the SO_2^- radical-anion does not change following the adsorption of C_6H_6 and the concentration of the $C_6H_6^+$ radical-cation is independent of the presence of adsorbed SO_2 molecules on the zeolite HM specimen. On the other hand, the adsorption of C_3H_6 on such a specimen containing adsorbed SO_2 molecules, some of which, as in the previous case, are in the form of SO_2^-, is accompanied by a sharp (by a factor of 5) increase of the concentration of SO_2^- and an appreciable decrease of the concentration of olefin radicals compared with their concentration on the clean zeolite HM.[19]

The results can be explained by the following processes occurring in the adsorption of C_3H_6 and C_6H_6:

$$RH + (III) \rightarrow \dot{R} + HO{-}Si\!\!\begin{array}{l}/\\ \backslash\end{array} \qquad (2)$$

$$\dot{R} + SO_2 \rightarrow R^+ + SO_2^- \ . \qquad (3)$$

Reaction (2) proceeds in the adsorption of both C_3H_6 and C_6H_6, but reaction (3) does not occur in the case of the $C_6H_6^+$ radical-cation, because its ionisation potential (9.90 eV) is higher than that of the C_6H_6 molecule (9.24 eV);[34] the concentration of SO_2^- ions does not therefore change on adsorption of C_6H_6. On the other hand, the ionisation potential of the olefin radical is lower than that of the initial molecule and reaction (3) is in this case accompanied by an increase in the concentration of the SO_2^- radical-anions. It is significant that an electron is definitely transferred to the SO_2 molecule from the olefin radical and not from the solid, because in the latter case an increase of the intensity of the signal of SO_2^- would have been observed as a result of the adsorption of C_6H_6.

The electron transfer from the olefin radical to the acceptor molecule described above is very similar to the formation of the SO_2^- radical-ion on the MgO surface in the adsorption of C_3H_6.[35] The following reactions probably occur in this system:

$$RH \rightarrow R^- + H^+ \ , \qquad (4)$$

$$R^- + O_2 \rightarrow \dot{R} + O_2^- \ , \qquad (5)$$

$$2\dot{R} + O_2 \rightarrow R{-}O{-}O{-}R \ . \qquad (6)$$

The difference between this reaction sequence and the previous one consists in the fact that the adsorption of C_3H_6 on the zeolite HM leads immediately to the formation of a radical and not a carbanion, but at the same time the introduction of O_2 is accompanied by the destruction of $\dot{R}$ via reaction (6) and the signal of the O_2^- radical-ion cannot therefore be detected in the EPR spectrum.

The influence of the introduction of various cations into the zeolite HM on the formation of radical species from different compounds, including olefins, has been examined.[36] It has been shown that the introduction of Be^{2+} and Ce^{4+} hardly influences the oxidation–reduction properties of the HM zeolite centres. It has been found that, despite their localisation in the large channel and their dipole–dipole interaction with the chemisorbed radicals, the introduction of Cu^{2+} cations lowers only slightly the concentration of the radical species formed at 20 °C from both aromatic compounds and from C_3H_6. The introduction into the zeolite HM of the ions Na^+, Mg^{2+}, Ba^{2+}, and Ni^{2+}, which are localised at sites which are not readily accessible to adsorbed molecules, leads to a considerable (by a factor of 10–30) decrease of the concentration of radicals. It has been suggested[36] that the formation of the oxidation–reduction centres in the zeolite HM is associated with the rupture of highly strained Si–O–Si(Al) bonds and the cations can have a stabilising effect on the mordenite skeleton.

VI. THE FORMATION AND REACTIONS OF RADICALS ON ZEOLITES OF THE ZSM TYPE

So far only one study devoted to the formation and reactions of radicals in the adsorption of unsaturated hydrocarbons on the zeolite H-ZSM-5 has been published.[37] The zeolite specimen was subjected to a preliminary heat treatment in an atmosphere of O_2 at 500 °C for 1 h; the reaction volume was then evacuated at the same temperature for 2 h, cooled to room temperature, and the specimen was transferred *in vacuo* into the cell of the EPR spectrometer, where the alkene and alkyne vapours were adsorbed at a low temperature.

Fig.12 presents the EPR spectra obtained at a reduced temperature for the initial zeolite ZSM-5 specimen and the specimen after the adsorption of but-2-yne and 3,3-dimethylbut-1-ene. The latter spectrum is isotropic (g = 2.0028 and a_H = 17.5 G) and has been assigned to the radical of

2,3-dimethylbut-2-ene arising as a result of the intramolecular rearrangement of 3,3-dimethylbut-1-ene. The EPR signal appearing as a result of the adsorption of but-2-yne on the zeolite ZSM-5 at −123 °C consists of seven components with a_H = 10.0 G, which is due to the presence in the molecule of two equivalent CH_3 groups, which rotate almost freely within the zeolite channel. On raising the temperature above 27 °C, the spectrum in Fig.12*c* is transformed into a nine-component spectrum (g = 2.009 and a_H = 6.60 G) and does not change further on raising the temperature to 200 °C.

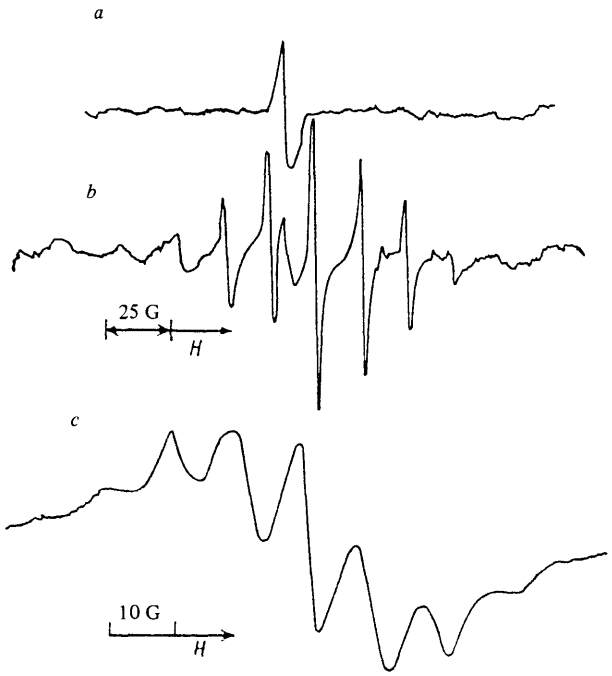
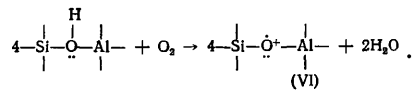
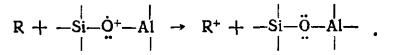


Figure 12. EPR spectrum of the lattice defects in the zeolite ZSM-5 at −150 °C (*a*) and the EPR spectra arising in the adsorption of 3,3-dimethylbut-1-ene at −150 °C (*b*) and but-2-yne at −123 °C (*c*) on the zeolite ZSM-5.

It has been suggested[37] that the spectrum in Fig.12*a* for the initial zeolite specimen is due to the appearance during the heat treatment of the zeolite in air at 500 °C of defect centres (VI) having a radical structure:

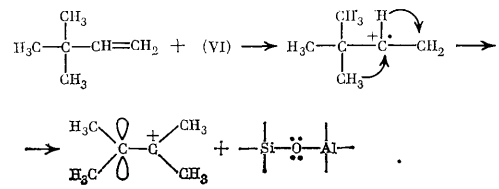


The centre (VI) obtained in this way is a hole in the oxygen atom of the zeolite lattice. According to the author,[37] the unpaired electron occupies a non-bonding molecular orbital of the oxygen atom, because at −196 °C a signal with an HFS characteristic of the reaction of the unpaired electron with the nuclear spin of the Al atom is not observed. Furthermore, the g-factor of the signal in Fig.12*a*, which is 2.0092, is equal to the g-factor of the signals due to the isoelectronic holes formed on X-irradiation of silicate and borate glasses. It has been suggested that the energy required for the appearance of such a radical centre is close to that necessary for the removal of an electron from the non-bonding orbital of the oxygen atom in the H_2O molecule, which is 12.61 eV according to photoelectron spectroscopic data. If this is true, then the positive radical centre is a powerful acceptor trap, in which the adsorbed molecule forms a radical-cation via a charge transfer mechanism:

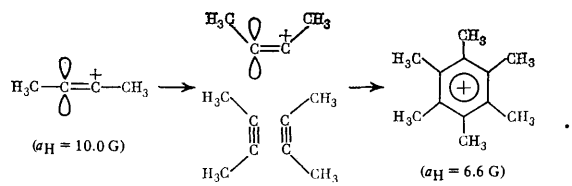


Unfortunately it is not stated in the above study[37] what is the concentration of such defect centres in the zeolite ZSM-5 and whether this concentration corresponds to the number of radical-cations formed. It is necessary to note that the nature of the centre (VI) and the character of the processes occurring on it are in essence identical to those for the centre (V) in the zeolite HM and the mechanism of the formation of radical-cations in the adsorption of olefins is the same as that discussed above.

The following mechanism has been proposed[37] for the formation of the radical and its isomerisation in the adsorption of 3,3-dimethylbut-1-ene on the centre (VI):



The change in the structure of the EPR spectrum of the adsorbed but-2-yne radical-cation on raising the temperature has been explained[37] by trimerisation accompanied by the formation of hexamethylbenzene radical-cations localised in the cylindrical channels of the zeolite ZSM-5:



Thus, in this case, as for the examples of the reactions of olefins on the zeolite HM discussed above, the final structure is an aromatic radical-cation. However, the author's hypothesis[37] that the hexamethylbenzene radical-cation is localised within the channel in the zeolite ZSM-5 is in our view erroneous, because in this zeolite the channel diameter, and not the channel radius as stated by Shih[37] is 5.8–6.0 Å; hexamethylbenzene molecules cannot be localised in such channels.

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The results of a few studies of the formation and reactions of the radicals arising in the adsorption of olefins on zeolites of types Y, HM, and ZSM-5 were examined above. Analysis of the available data shows that the adsorption of olefins of different types at room temperature on cationic and decationated forms of zeolites of the faujasite type is accompanied by the appearance of EPR spectra with virtually identical parameters. EPR spectra of identical structure also arise in the adsorption of various olefins at 20 °C on cationic, decationated, and dealuminated forms of mordenite,

but their parameters differ significantly from those observed in the adsorption of the same olefins on faujasites.

In the discussion of the results it was shown that the radicals formed in the adsorption of olefins on mordenites at 20 °C are secondary radical species arising due to oligomerisation processes and that both oxidative and Brønsted centres participate in the formation of these species. The adsorption of olefins on mordenites at low temperatures is accompanied by the formation of primary radicals characterised by individual EPR spectra. An important feature of mordenites is their ability to form selectively aromatic structures, giving rise to EPR spectra with the characteristic HFS, from compounds of different classes on zeolite lattice elements with a specific geometry.

Despite the considerable advances made, many problems still remain unsolved. The chemical nature of the radicals formed on faujasites has not been elucidated and in particular it is not known whether these radicals are primary adsorbed species or whether they are formed later as a result of subsequent chemical reactions. The mechanism of the activating influence of oxygen has not been established and its role in the formation of radicals has not been elucidated. Furthermore, the fundamental question of the nature of the oxidative centres involved in the formation of radicals still remains open, particularly for faujasites.

The solution of these problems is important not only in itself but it is also essential for the understanding of the mechanisms of the catalytic processes involving olefins and in particular on high-silica zeolites, for which one cannot rule out the possibility of an important role of reactions involving radical species.

It is noteworthy that the application of the EPR method to the elucidation of the mechanisms of the thermal transformations of compounds of different classes, including olefins, adsorbed on zeolites is important also for the analysis of the nature of the "coke" deposits formed under these conditions, which play a decisive role in the deactivation of zeolite catalysts.

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The Structure and Valence Isomerisation of Antiaromatic Compounds

M.N.Glukhovtsev, B.Ya.Simkin, and V.I.Minkin

Various criteria of aromaticity and their relation with molecular structure are discussed. The characteristics of the quantum-chemical calculations of the electronic structure and geometry of antiaromatic molecules, determined by the specific structure of their potential energy surfaces corresponding to the ground and lowest excited states, are analysed.
The bibliography includes 264 references.

CONTENTS

I. Introduction 54
II. The structure and valence isomerisation of antiaromatic $(CH)_n$ polymethines and their hetero-substituted derivatives 60
III. Non-alternant [*n*]annuleno[*n*]annulenes containing internal or perimetric $4m\pi$-electron rings 68
IV. Alternant [*n*]annuleno[*n*]annulenes containing internal or perimetric $4k\pi$-electron rings 71

I. INTRODUCTION

Among the theoretical ideas of organic chemistry, it is difficult to find another concept like aromaticity which is as general and plays as important a role in systematic treatment of structural characteristics, stability, physical properties, and reactivity and is at the same time so vaguely but physically unambiguously defined. Indeed, the brief survey below of the unceasing attempts to canonise the concept of aromaticity demonstrates the possibility of enclosing it within a rigorously fixed framework whatever the theoretical and experimental approaches employed.

This factor is the cause of the unceasing controversy whether or not the term "aromaticity" is legitimate. Binsch[1] expressed an extreme point of view. In his paper "Aromaticity—an Exercise in Chemical Gibberish" he defines the main purpose of the concept of aromaticity simply as an "alibi for a certain aura of intellectual respectibility necessary to the investigator when the conclusions arising from his work are on the edge of banality". In fact, it is impossible to isolate a single physically defined structural or energetic parameter which would characterise the degree of aromaticity of a molecule or ion. However, many other concepts of theoretical organic chemistry, whose fruitfulness arouses no doubts, would not withstand such a rigorous criterion. It is sufficient to recall concepts such as isomerism,[2,3] tautomerism,[3,4] conformation, and configuration.[5] The very concept of molecular structure is far from unambiguous when subjected to a rigorous analysis.[5,6]

Numerous reviews[7-11] and monographs[12-16] have been devoted to the analysis of the development of the concept of aromaticity. The energetic aspect, the relative stability of the structure, is nowadays associated primarily with aromaticity or aromatic character. Although individual attempts have been made to extend the concept of aromaticity to acyclic compounds (for example, the concept of Y-aromaticity has been introduced[17]) and saturated compounds (σ-aromaticity[18]), in general it is used to describe the enhanced stability of a particular type of cyclic structures relative to acyclic structures.[9,19,20] Finally, a tendency has become increasingly clear to relate the enhanced stability of aromatic structure to the closed nature of its electron shell.[17]

The synthesis and theoretical studes of various types of cyclic structures, for which the above conditions are realised and which therefore possess an increased relative stability, have led to the formation of a whole series of new structural concepts refining the concept of aromaticity and demonstrating its fruitfulness. The scheme illustrated in Fig.1 provides a by no means complete representation of various structural types of aromaticity.

The task of the present review is to examine the problem of antiaromaticity, mainly from the standpoint of its structural aspect. Since the concept of antiaromaticity is set against that of aromaticity, it is evident that the main feature of antiaromaticity is cyclic destabilisation, i.e. the energetically unfavourable nature of a planar cyclic structure of a conjugated molecule or ion with declocalisation of π-bonds.

As will be shown below, the main cause of the antiaromatic character of a structure is specific features of the structure of the electron shells of the corresponding cyclic conjugated compounds. A detailed understanding of these features involves a fairly profound theoretical study of the problem, requiring the application of the most refined methods of modern quantum chemistry. Because of the instability of antiaromatic compounds and the consequent difficulty of their experimental study, the quantum-chemical approach assumes a particular importance in this instance.

The data obtained with the aid of quantum-chemical calculations can be used to identify the most promising trends in preparative research and to investigate the details of the mechanisms of reactions of antiaromatic compounds. In view of this, in the present review attention is concentrated on the theoretical study of the structures of antiaromatic compounds and it is endeavoured to demonstrate to what extent the combination of the theoretical and experimental methods of organic chemistry has been fruitful in this instance.

The review deals with the principal types of antiaromatic compounds—monocyclic polymethines $(CH)_m$ with $4n\pi$-electrons, annulenoannulenes, and their heterosubstituted derivatives. Various compounds classified as antiaromatic contain fragments corresponding to these structures. In view of this, the observed characteristic features of the electronic and geometrical structures and of valence isomerisations of antiaromatic compounds are fairly general.

The instability of antiaromatic compounds is responsible for their tendency to undergo valence isomerisation reactions and rearrangements, as a result of which the energetically unfavourable planar conjugated bond system breaks down. Quantum-chemical data made it possible to interpret the instability of antiaromatic compounds from the standpoint of the properties of the corresponding potential energy surfaces (PES), which determine the wide variety of types of valence isomerisations; the PES of antiaromatic compounds are characterised by relatively low barriers to isomerisation—the proximity of the surfaces corresponding to excited states which as a rule gives rise to electronic lability of the molecule.[29-32] These features of the PES of antiaromatic compounds hinder the application of traditional computational schemes, which do not always yield equivalent results.

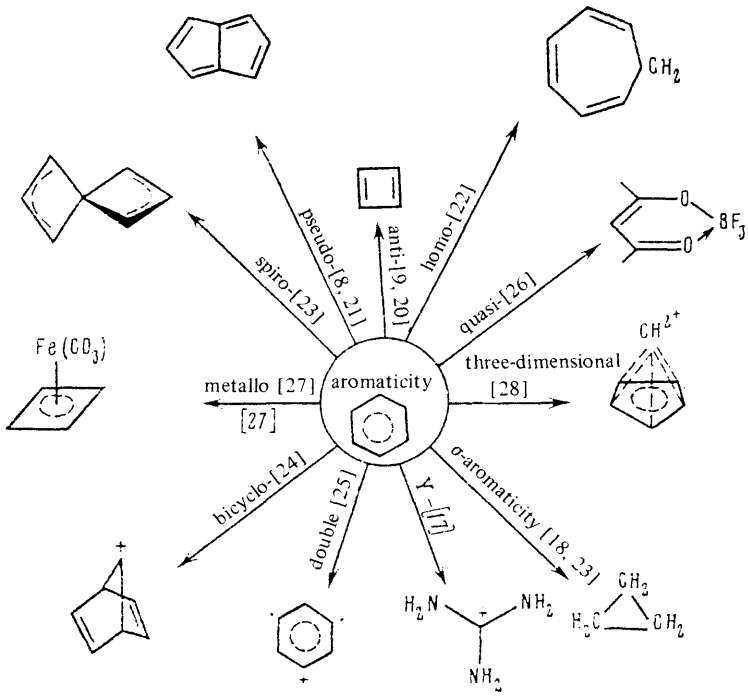


Figure 1. Illustration of the wide variety of aspects of the concept of aromaticity. Structures corresponding to a particular type of aromaticity are presented.

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

Because of this, the class of antiaromatic compounds constitutes a kind of "touchstone" for the estimation of the limited applicability of a particular theoretical method and makes it possible to elucidate its limitations and scope for further improvement.

1. Criteria of Aromaticity and Antiaromaticity

An unambiguous criterion which could be used to classify particular compounds—aromatic or antiaromatic—does not exist. The criteria based on reactivity data characterise the kinetic stability and are determined by the properties not only of the ground state of the molecule but also those of the transition state in the reaction considered. The capacity to undergo electrophilic substitution reactions, which is frequently regarded as the most characteristic feature of aromatic compounds,[13] cannot always be used as a sufficiently reliable sign of aromaticity.[33] In their monograph "Facts and Theories of Aromaticity", Lewis and Peters[16] concluded on the basis of a detailed discussion of various interpretations of the term "aromaticity" that the most general definition reduces to the following: "an aromatic molecule is a molecule which resembles benzene". Even in this definition, it is necessary to establish which feature of similarity is the most important. In the present reivew the structural-energetic criterion has been adopted for this purpose: a conjugated compound is aromatic if the delocalisation of π-electrons stabilises its cyclic structure relative to the corresponding acyclic polyene structure (for example, benzene and hexa-1,3,5-triene). On the other hand, in the case of a greater stability of the acyclic reference structure (cyclobutadiene and buta-1,3-diene) the given system is classified as antiaromatic.

Quantitative estimates of the degree of aromaticity or antiaromaticity are based on the concept of resonance energy.

(a) Energetic criteria of aromaticity and antiaromaticity. The resonance energy. Hückel[34] showed that the molecule or ion with a monocyclic structure is stabilised when the bonding π-orbitals are completely filled with electrons and the non-bonding and antibonding molecular orbitals (MO) are unoccupied. The fulfilment of these conditions leads to the familiar $(4n + 2)$ rule for the number of π-electrons in an aromatic monocyclic compound. On the other hand, annulenes with $4n$ π-electrons in the ring have an open π-electron shell. The cyclic delocalisation of π-electrons in these systems leads to the destabilisation of the structure. Consequently, $[4n]$-annulenes must be classified as antiaromatic systems.

The general concept—the requirement that all the bonding MO are completely filled and the remaining MO are unoccupied—proved to be fruitful also for three-dimensional systems [polyhedral carbaboranes,[35] pyramidal structures $(CH)^{n+}_{n+4}$,[36] and organometallic clusters,[37] for the determination of the stability of which specific electron count rules have been proposed[38,39]]. This concept has been extrapolated also to acyclic conjugated molecules. For example, the stable guanidinium cation, which contains six π-electrons, has been assigned to the class of so-called molecules with a centre of aromaticity (Y-aromaticity[17]), while trimethylenemethane (four π-electrons) can be regarded as an antiaromatic system in this sense.[31]

The contribution of conjugation to the energy of the molecules is characterised by the Hückel resonance energy (HRE), which is defined in terms of the Hückel approximation[40] as the difference between the total π-electron energies of the conjugated molecule and a system consisting of m

isolated double bonds present in the classical (Kekulé) structure of the conjugated molecule:

$$\mathrm{HRE} = E_\pi^m - mE_\pi(\mathrm{C{=}C}), \qquad (1)$$

where E_π^m is the π-electron energy of the conjugated molecule.

However, estimates of aromaticity with the aid of the HRE did not prove to be entirely satisfactory. Thus, in conformity with Eqn.(1), the degree of aromaticity should increase with increasing size of the π-electron system, which conflicts with certain experimental data. For example, the kinetic stability of polyacenes diminishes on successive linear annelation (pentacene and hexacene readily interact with atmospheric oxygen[43]). In a number of instances unduly high HRE correspond to antiaromatic molecules,[44] for example, the HRE of pentalene (2.46β) is higher than for benzene (2β).

Dewar[45,46] developed a more rigorous scheme for the estimation of the resonance energies of cyclic conjugated structures. He adopted as the reference structure a polyene in which the numbers of the σ- and π-bonds are equivalent to those in the cyclic compound and not the system of isolated π-bonds adopted when Eqn.(1) is used. Using the approximation assuming the additivity of the bond energies in acyclic polyenes,[47] it is possible to calculate the total energy of any acyclic or cyclic polyene with localised double bonds by adding together the energies of all the bonds. The Dewar resonance energy (DRE) is defined as the difference between the heat of formation of a given conjugated molecule and the heat of formation calculated for the classical (Kekulé) reference structure:

$$\mathrm{DRE} = -(\Delta H^m - \Delta H_{\mathrm{add}}), \qquad (2)$$

where ΔH_{add} is the heat of formation calculated for the model reference structure (the minus sign is included because the values of DRE for aromatic systems are assumed to be positive (see Dewar,[45] p.480). For example, for benzene we have $\Delta H_{\mathrm{add}} = 3E_1 + 3E_2 + 6E_{\mathrm{C-H}}$, where E_1 and E_2 are parameters representing the energies of the "polyene" single and double bonds. Thus DRE can be expressed in a form more convenient for comparison with the HRE:

$$\mathrm{DRE} = -(E_\pi^m - (n_1E_{1\pi} + n_2E_{2\pi})) \qquad (3)$$

where n_1 and n_2 are the numbers of single and double bonds in the Kekulé structure of the π-electron system considered and $E_{1\pi}$ and $E_{2\pi}$ are the π-electron energies of the "polyene" single and double bonds.

The method for the calculation of the resonance energies described above makes it possible to take into account more accurately the contribution of cyclic conjugation to E_π. Furthermore, since the calculation of the DRE is based on the scheme of the Pariser–Parr–Pople (PPP) method modified by Dewar and de Llano,[42] which makes it possible to take into account the contribution of σ-bonds, the values of DRE in Eqn.(2) contain a correction for the energy of the contraction (extension) of the σ-bonds in the cyclic conjugated compound relative to the model structure. The values of DRE are satisfactorily correlated with experimental stability data[44] (furthermore in the case of annulenes, for example, a series of correlations have been observed between the physicochemical properties and the resonance energy, in particular between the $\Delta G^{\neq}$ for the Diels–Alder reaction with maleic anhydride and the difference between the corresponding resonance energies).

On the basis of the Hückel method, Hess and Schaad developed a scheme for the calculation of the resonance energy (HSRE) in which account was taken of the differences between the immediate environments of the bonds (C–C and C=C).[45,46]

The sharp increase of the number of empirical parameters for heteroatomic molecules must be included among the disadvantages of the DRE and HSRE definitions. Furthermore, the values of DRE and HSRE can be found only for molecules for which it is possible to construct Kekulé structures and hence the above definitions are inapplicable to radicals, ions, and non-classical structures (see, however, Hess and Schaad[47]).

The definition of the topological resonance energy (TRE),[48–50] based on the employment of the Hückel theory and the methods of the theory of graphs,[51] is free from these disadvantages. The concept of the TRE is applicable to any conjugated system, including ions, radicals, and radical-ions.[52,53]

The TRE, defined by the formula

$$\mathrm{TRE} = \sum_j (g_jx_j - g_j^{\mathrm{acycl}}x_j^{\mathrm{acycl}}) \qquad (4)$$

(g_j are the filling numbers for the filling of π-orbitals by electrons in the ground state, x_j the roots of the characteristic polynomial for the conjugated system, and x_j^{acycl} and g_j^{acycl} refer to the acyclic polynomial[48–50] corresponding to the given molecular graph), characterises the cyclic conjugation energy in the given molecule or ion.

We emphasise that, in estimating the degree of aromaticity with the aid of the TRE, there is no need to select a suitable reference structure. Furthermore, the acyclic polynomial used in the definition of the TRE need not correspond to any real structure which can be represented in the traditional way. This is both an advantage and a disadvantage of the TRE as a criterion of aromaticity, since the concept of the TRE is not linked directly to the concepts of structural chemistry familiar to chemists. In a number of instances, the estimates of the TRE are nevertheless unsatisfactory.[54–56] Thus the TRE for cyclobutadiene (−1.226β) has been obtained on the assumption that $g_1 = g_2 = 2$. However, according to Hund's rule, it must be assumed that $g_1 = 2$ and $g_2 = g_3 = 1$; the TRE then obtained is +0.304β, i.e. cyclobutadiene then appears to be actually more aromatic than benzene.

Table 1. The values of HRE, DRE, HSRE, and TRE for certain annulenes, annulenoannulenes and monocyclic conjugated ions (all the resonance energies have been normalised per π-electron in the calculation).

Compound	HRE, β units (Refs.34, 41)	DRE, eV (Refs.42, 44)	HSRE, β units (Refs.45–47)	TRE, β units (Refs. 48–50, 52, 53)
Cyclobutadiene	0.000	−0.1335	−0.268	−0.3065
Benzene	0.333	0.1450	0.065	0.046
Cyclo-octatetraene	—	0.0542	−0.0609	—
Propalene	—	—	−0.100	—
Pentalene	0.307	0.0008	−0.018	−0.027
Heptalene	0.302	0.0078	−0.004	−0.012
Butalene	—	−0.0457	−0.067	−0.1007
Octalene	—	−0.0007	0.007	—
Cyclopropenyl anion	—	—	−0.423	−0.366
Cyclopentadienyl cation	—	—	−0.114	−0.153

The values of DRE, HSRE, and TRE for benzene and certain antiaromatic compounds are listed in Table 1 (to facilitate comparison, the RE for different systems have been calculated per π-electron). The values of TRE normalised in this way are linked to the HSRE by the relation[57]

$$\mathrm{TRE} \cong \mathrm{HSRE} + (0.69/N)\ln K, \qquad (5)$$

where N is the number of π electrons, K the number of Kekulé structures; the values of TRE and HSRE are calculated per π electron.

The heats of isodesmic[58] reactions, characterising the stability of the given cyclic systems relative to the corresponding acyclic compounds with the same types of single and double bonds, have also been used to determine the resonance energy. Thus the heats of the given reactions can be used to estimate the energy of cyclic conjugation in the given system, reflecting thereby its aromatic or antiaromatic character,[60] for example (the values of ΔH are given in kJ mol^{-1}):

$$+ 4CH_4 \rightarrow 2CH_3{-}CH_3 + 2CH_2{=}CH_2 \qquad (6)$$

ΔH = —294.5 [MINDO/3 (Ref.59)]; —217.1 (MNDO); —268.6 [STO-3G (Ref.60)]; —278.2 [4-31G (Ref.60)]; —284.1 [6-31G//3-21G (Ref.61)]†;

$$+ 6CH_4 \rightarrow 3CH_3{-}CH_3 + 3CH_2{=}CH_2 ; \qquad (7)$$

ΔH = 30.4 (MINDO/3); 154.8 (MNDO).

(b) Magnetic criteria of aromaticity and antiaromaticity. It has been suggested that a compound be defined as aromatic if induced diamagnetic π-electron ring currents are maintained in its molecule (diatropic system). The ring current influences the chemical shifts in the ^{1}H NMR spectra and the current itself is used as a quantitative measure of the aromaticity of the compound. On the other hand, paramagnetic ring currents (paratropic systems) are characteristic of antiaromatic compounds, for example [4n]annulenes (see the relevant reviews[62,63]).

In the case of [4n + 2]annulenes there is a simple relation between the resonance energy per π-electron (RE/π-E in β units) and the system of π-electron ring currents I [64–66]:

$$RE/\pi\text{-}E = \frac{\pi^2 I}{kS}, \qquad (8)$$

where S is the area of the ring; for benzene, it has been assumed that $S = 1$, $k = 3$;[64] $k = 4$.[65]

In addition a linear correlation has been observed between the difference between the chemical shifts of the signals due to the external and internal protons for $\tau_{ext} - \tau_{int}$ in the ^{1}H NMR spectra of [n]annulenes and the value of RE/π-E:[67]

$$\frac{(\tau_{ext} - \tau_{int})}{S} = m(RE/\pi\text{-}E), \qquad (9)$$

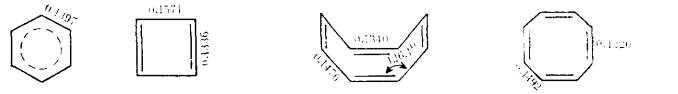
where m is a constant.

However, for non-alternate hydrocarbons and for heterocyclic systems, the relation between the resonance energy and the magnetic criteria is not sufficiently defined.[64] Furthermore, the results of calculations of ring currents for antiaromatic systems depend greatly on the method employed (see, for example, Mallion[62]).

The use of magnetic parameters as exhaustive criteria has been subjected to serious criticism.[16,62] We may point out, for example, that the manifestation of diatropism does not necessarily indicate a tendency towards electrophilic substitution reactions or even the stabilisation of the cyclic conjugated system.[66] In many cases the system may be diatropic and antiaromatic, for example, bicyclo[6.2.0]-decapentane.[68]

†Here and henceforth the abbreviations proposed by Pople are used; the numerals in brackets indicate that a non-empirical calculation has been carried out in terms of, for example, the 6-31G basis set, for the geometry optimised in terms of the 3-21G basis set.

(c) Structural criteria of aromaticity and antiaromaticity. The most distinctive structural characteristics of the benzene molecule are its planarity and complete equalisation of the C–C bond lengths. In conformity with the structural criterion, analogous properties are to be expected for aromatic molecules. On the other hand, for antiaromatic molecules, in which the cyclic conjugation destabilises the structure, one may expect a tendency towards the localisation of double bonds, i.e. towards the breakdown of the equalisation of the C–C bond lengths.



[according to results of *ab initio* calculations (Ref.69)] [according to electron diffraction data (Ref.70)] [according to results of *ab initio* calculations (Ref.71)]

It has been suggested that the molecule be regarded as aromatic when the lengths of the carbon–carbon bonds are in the range 0.136–0.143 nm, i.e. are close to the value of 0.1397 nm in benzene, and should be regarded as a polyene when the C=C bond length is in the range 0.134–0.135 nm, while the C–C bond length is 0.144–0.1475 nm.[16] A quantitative character has been given to this criterion. The degree of aromaticity has been estimated from the means square deviation of the carbon–carbon bond lengths:[72]

$$\delta = \frac{\sum_{rs} (d_{rs} - \bar{d})^2 / \bar{d}^2}{n}, \qquad (10)$$

where d_{rs} is the length of the bond between the atoms r and s and $\bar{d}$ is the average length of n bonds (Å).

The aromaticity index A was then determined[72] from the formula

$$A = 1 - 225\delta . \qquad (11)$$

Subsequently the expression for A was modified in order to take into account the requirement for the equalisation of the distribution of electron density along the ring bonds of the aromatic molecule.[73] However, difficulties then arise in the case of molecules such as those of azulene owing to the considerable length of the transannular bond and in the case of heterocyclic conjugated molecules. Developing the criterion of bond length equalisation for the definition of aromaticity, Kruszewski and Krygowski[74] suggested that two aromaticity indices, based on the harmonic oscillator model (HOMA), be introduced. The value of HOMA$_d$ is determined by the length d(Å) of the carbon–carbon bonds:

$$HOMA_d = 1 - \frac{a}{n}\sum_{r=1}^{n} (X_r - 1.397)^2 \qquad (12)$$

where $a = 98.89$, X_r is the length of the rth bond, and n is the number of bonds. HOMA$_d$ = 1 has been obtained for the structure of benzene with D_{6h} symmetry and HOMA$_d$ = 0 has been found for the molecule with D_{3h} symmetry. Thus HOMA$_d$ reflects the increase of the energy of the π-electron system when the bond lengths deviate from the value in benzene (1.397 Å).

The index HOMA$_p$ is determined by the bond orders:

$$HOMA_p = 1 - \frac{3.66}{n}\sum_{rs}^{n} \left(\frac{2}{3} - P_{rs}\right)^2 , \qquad (13)$$

where P_{rs} is the order of the bond between the atoms r and s.

The planarity of the molecule is usually regarded as a characteristic feature of aromatic systems.[13] However, the non-planar character of the structures of [4n]annulenes can

hardly be interpreted solely as a consequence of antiaromaticity,[75,76] because the strains in the σ-electron system can play a decisive role in the breakdown of planarity. Cyclooctatetraene has a non-planar structure with D_{2d} symmetry but its π-electron energy is a minimum for a planar configuration and the non-coplanar distortion leads to an increase of this energy.[75] The non-planar character of the carbon skeleton for cyclo-octatetraene and of its derivatives is due to angular strains which arise in the planar σ-electron system (their contribution to the enthalpy of the transition to the D_{2d} configuration is ~85%).[77,78]

Thus one should not completely identify antiaromaticity with the tendency towards the breakdown of the planar structure of the molecule. A molecule which can be classified as antiaromatic can deviate only slightly from a planar conformation, as, for example, for 1,5-bisdehydro[12]annulene,[76] and at the same time the properties of the σ-electron system can determine the non-planar structure also in the case of aromatic compounds. For example, non-empirical calculations for the cyclobutadiene dication (two π electrons) point to a non-planar structure with D_{2d} symmetry.[79,80] On the other hand, calculations by the MINDO/3 method have shown[81] that a saddle point and not a minimum on the potential energy surface of cyclobutadiene (C_4H_4) corresponds to the non-planar structure of its molecules, which have the same symmetry.

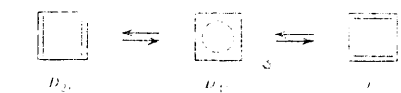
Thus the structural criterion of antiaromaticity is apparently most correctly treated as the energetic preference for a planar structure with alternating bond lengths as compared with a planar highly symmetrical structure with equalised carbon–carbon bond lengths. The generality of this structureal criterion is confirmed by the results of Nakajima and Binsch et al., who developed the theory of lattice instability in a series of studies (see the relevant reviews[82,83]).

In order to determine the stability of a highly symmetrical planar configuration of the molecule relative to distortions leading to planar structures of lower symmetry, it is necessary to estimate the force constant of the corresponding normal vibration Q_i which causes the deformation of the highly symmetrical configuration. A conjugated cyclic system is aromatic if the "fixation of double bonds" of the first or second order is not observed (in the first-order bond fixation, the symmetry of the σ-skeleton does not change in contrast to the second-order bond fixation).[83] The second-order double bond fixation is characterised by a minimum eigenvalue λ of the bond–bond polarisability matrix and the corresponding eigenvector determines the symmetry of the distortion. If λ_{max} (in units of β) is less than a critical value $\lambda_{cr} = 1.22$, then the system is stable in relation to distortions leading to the breakdown of the equalisation of bond lengths. For example, the minimum force constant for the in-plane vibrations of benzene corresponds to a distortion b_{2u} to give the D_{3h} structure, but $\lambda_{max} = 0.791 < \lambda_{cr}$ and a distortion of this kind is not realised. On the other hand, for pentalene and heptalene the calculated λ_{max} exceed λ_{cr} and a dynamic alternation of bond lengths,[83] analogous to the topomerisation of the D_{2h} structure of cyclobutadiene,[84,85] should obtain for such compounds, which makes it possible to classify pentalene and heptalene as antiaromatic systems.

The criterion of the lattice instability is consistent with the criteria based on the resonance energies and magnetic properties.[64]

The degree of instability of the molecular configuration and the possibility of a reduction of symmetry are caused by the second-order Jahn–Teller effect, which depends on the difference $\Delta E = E_1 - E_0$ between the energies of the ground and first excited singlet states.[82] The following criterion of the instability of the geometrical configuration of the molecule has been formulated: if the quantity ΔE calculated for a given structure with equalised bond lengths is less than the empirically selected quantity 1.2 eV, then the force constant of the in-plane skeletal vibration will assume a negative value, giving rise thereby to a tendency towards a distortion resulting in a less symmetrical structure with alternating carbon–carbon bond lengths.[82,86,87] Thus $\Delta E = 0.35$ eV has been obtained for the pentalene structure with D_{2h} symmetry and this structure is unstable in relation to distortions giving rise to a structure with C_{2h} symmetry.

Thus a minimum on the potential energy surface does not correspond to a highly symmetrical configuration of the singlet state of antiaromatic molecules. On the other hand, there are minima on the potential energy surface corresponding to structures with reduced symmetries involving alternating bond lengths, which are interconverted via a multiplicity of valence isomerisation modes. The topomerisation of structures with alternating bond lengths is then the main process:



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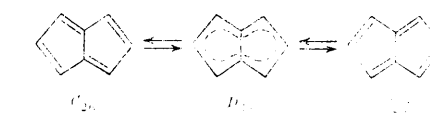


(15)

For benzene, the structure with D_{6h} symmetry corresponds to a minimum on the potential energy surface for the C_6H_6 system. For example, the structure of the singlet state of cyclobutadiene with D_{4h} symmetry is the transition state in the topomerisation reaction of the D_{2h} configuration (Fig. 2).[88–90]

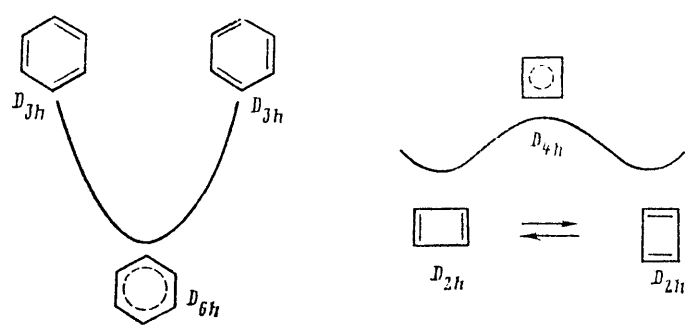


Figure 2. Potential curves for benzene and cyclobutadiene molecules along the coordinate corresponding to the shift of the double bonds.[3] In the case of benzene a skeletal vibration is observed in the Raman spectrum at 1585 cm^{-1}. For cyclobutadiene, the topomerisation of the D_{2h} structure takes place.

The multiplicity of other proposed aromaticity–antiaromaticity criteria,[12–16,91–96] and their interrelations[97] cannot be discussed within the framework of the present review. Furthermore, almost all the remaining definitions are to some extent derived from the fundamental criteria of aromaticity–antiaromaticity considered above.

We may note that the application of the concept of resonance energy and magnetic criteria to antiaromatic molecules does not in fact always lead to definite conclusions.[55,62]

2. Characteristic Features of the Calculation of the Electronic Structure of Antiaromatic Molecules

The complex relief of the potential energy surfaces of antiaromatic molecules and the closeness of the energy surfaces for the ground and lowest excited states, which in many instances leads to their touching and even intersecting, are all factors which impose more stringent requirements on the rigour of the quantum-chemical calculations of the electronic structures of antiaromatic molecules. When the SCF MO method is used, one encounters the problem of the stability and multiplicity of the Hartree–Fock (HF) solutions.[98–114]

In this connection it is necessary to note two aspects of the problem. The first involves the methodology of the correct selection of the computational scheme which can yield specific results for antiaromatic molecules. The second involves the interrelation between the so-called singlet instability of the HF solutions for antiaromatic molecules and the lattice instability, which we mentioned in the previous section as one of the structural criteria of aromaticity–antiaromaticity. The schemes for the calculation of the stabilities of solutions have been examined in a number of studies.[99,107–109] They reduce to the evaluation of the eigenvalues of the instability matrices, whose elements are determined from the familiar formulae for the matrix elements of the HF Hamiltonian between singly excited states and between the ground and doubly excited states.[99]

It is possible to discover a series of instability levels[108–111] which determine the concrete form of the instability matrix. In the case of a closed shell the singlet and triplet (non-singlet) instabilities are treated within the framework of the restricted Hartree–Fock method (RHF), which presupposes identical spatial wave functions for electrons with different spins. The singlet instability is the instability in the variations of the overall wavefunction with retention of the twofold occupation of the orbitals. The triplet instability is one corresponding to the abandonment of the restriction in the RHF method imposed by the requirement for the twofold occupation of the orbitals and to variations characteristic of the unrestricted Hartree–Fock method (UHF).

The triplet instability of the solutions obtained in the calculation by the RHF method is a sufficient (but not necessary) condition for the existence in the calculation by the UHF method of a solution with a lower energy.[99,108] This type of instability is much more common than the singlet instability. The instability of the relative occupation of the MO [the so-called filling up (FU) instability[107]] where the filling of the highest orbitals can lead to solutions with a lower total energy, to the breakdown of the Aufbau-principle of the filling of energy levels,[100] is of special interest.

If the solution by the RHF method is unstable, it is necessary to take into account correlations effects.[115] For a correct description of the electronic structures of antiaromatic molecules, there exist in this instance two alternative procedures.[116] Firstly, remaining within the framework of the one-determinant approach, one can employ MO of lower symmetry than that of the nuclear skeleton, while in the presence of triplet instability one can employ the UHF method. This procedure makes it possible to obtain results which agree well with experimental data, in contrast to those based on the use of fully symmetrical solutions (see, for example, Karpfen and Petkov[117] and Canuto et al.[118]). In the presence of triplet instability, the transition to the UHF approximation makes it possible to describe the multiplicity of the electronic state of the highly symmetrical configurations of antiaromatic molecules.[119–122] For example, analysis of the stability of the solution for cyclobutadiene obtained by the UHF method indicates a singlet ground state having a D_{4h} structure.[119,122] On the other hand, the cyclopropenyl anion (D_{3h}) and the cyclopentadienyl cation (D_{5h}) have a triplet ground state.[119] Thus the study of the character of the stability of the HF solution permits qualitative conclusions about the nature of the electronic ground states of the given molecules which are fully confirmed by non-empirical calculations taking into account the electronic correlation energy.[88–90]

Another procedure for taking into account correlation effects is also possible, involving the superposition of configurations made up of MO with corresponding symmetries or involving the use of multiconfiguration self-consistent field methods (MC SCF). Although this approach requires the allowance for a large number of configurations and involves a considerable consumption of computer time, nevertheless it is perhaps the most preferable. In relation to the cyclopropenyl anion, cyclobutadiene, the cyclopentadienyl cation, and other antiaromatic molecules, the multiconfiguration approximation was developed further by Borden and Davidson (see the relevant reviews[29,31] and the literature quoted therein).

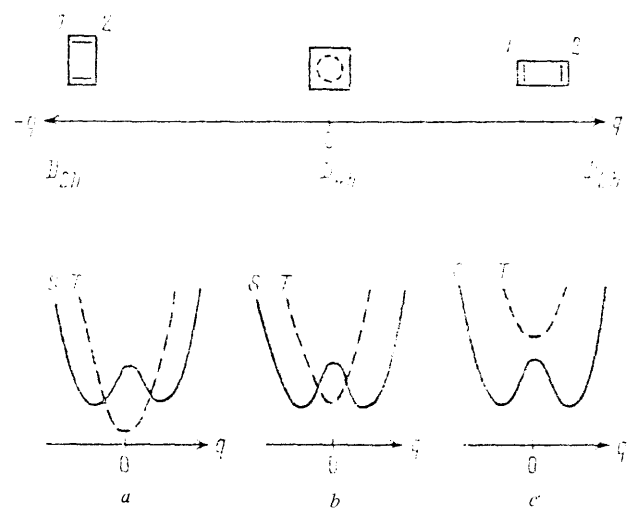


Figure 3. The forms of cross-sections through the potential energy surface for C_4H_4 along the locus of the minimum energy of the reaction (LMER) involving the topomerisation of the cyclobutadiene structure with D_{2h} symmetry (q is the reaction coordinate).

The second structural aspect of the problem of the instability of the HF solutions is determined by the relation between the singlet instability of solutions by the RHF method and lattice instability. The singlet instability has been revealed by the results of calculations by semiempirical methods of the PPP type for aromatic hydrocarbons only when unrealistic values of the resonance integral β were used.[123] However, for antiaromatic molecules the singlet instability of the RHF

solutions has been found even for values of the resonance integral β close to the standard values.[124,125] The singlet instability entails the existence of a solution with an electron distribution corresponding to a reduced symmetry, which gives rise to a tendency towards the distortion of the highly symmetrical geometrical configuration (lattice instability)[126-129] and determines the symmetry of this distortion.[129] The relation between the matrix of the singlet instability and the expression for the force constant when the molecular configuration is distorted as a consequence of the second-order Jahn–Teller effect has been demonstrated.[130]

Thus the singlet instability in the solutions by the RHF method for antiaromatic molecules is responsible for the possibility of the lattice instability, which is one of the structural criteria of aromaticity-antiaromaticity and makes it possible to predict a number of characteristics of the potential energy surface. The presence of the single instability should be regarded as an indication of the necessity to correct the initial hypothesis concerning the form of the nuclear configuration.[131] The possibility of a dynamic process involving the isomerisation of antiaromatic molecules is generally speaking an essential consequence under these conditions of the singlet instability and must be investigated in each specific case. The quantum-chemical calculation of the potential energy surfaces of antiaromatic compounds, to the results of which the next Section of this review is devoted, assumes particular importance in this connection.

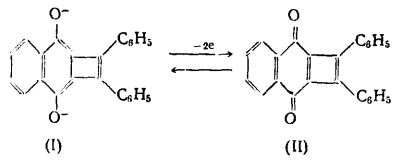
II. THE STRUCTURE AND VALENCE ISOMERISATION OF ANTIAROMATIC $(CH)_n$ POLYMETHINES AND THEIR HETERO-SUBSTITUTED DERIVATIVES

1. Cyclobutadiene

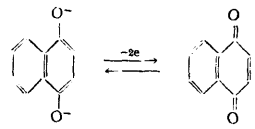
Cyclobutadiene (CBD) is the key structure in the theory of antiaromatic systems. Just as the benzene molecule is a prototype of an aromatic system, CBD is regarded as an example of a system which is antiaromatic not only on a relative scale (compared with the corresponding model system), but also on the absolute scale,[132] bearing in mind the degree of localisation of the molecular π orbitals. This implies that the electronic-structural properties of CBD are directly opposed to those of benzene. The bond conjugation in the four-membered ring of CBD causes a sharp destabilisation of the structure which is expressed in negative resonance energies for CBD (Table 1), the localisation of the double bonds in the ring, a tendency towards reactions involving addition to the double bonds, and the stereochemical non-rigidity of the CBD molecule associated with the fluctuations of the positions of the π bonds in the molecule.

Monographs and reviews have been devoted to CBD.[29,31,133-135] Here we shall briefly consider the principal manifestations of the antiaromaticity of CBD by comparing the thermodynamic stabilities of CBD and its derivatives, the tendencies towards isomerisation, and the structural characteristics.

The resonance energies of CBD calculated by different procedures (Table 1) may be compared with the experimental data. The latter are based on a comparision of the energy relations of isotypical reactions, some of which lead to the formation of the [4]annulene fragment, with other reactions in which this fragment does not arise. For example, a study has been made[9,136] of the reversible electrochemical oxidation-reduction of the quinones (II) and (IV):



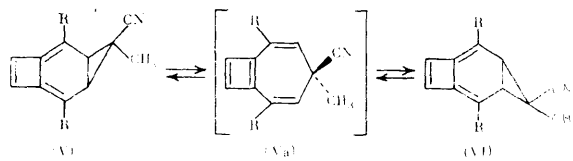
(I) (II) (16)



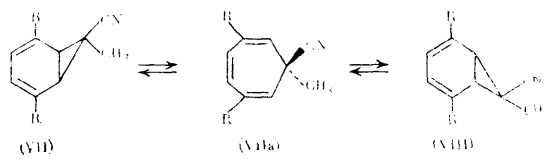
(III) (IV) (17)

The much higher oxidation potential of compound (I) compared with that of compound (III) has been interpreted[9,136] as the manifestation of the characteristic features of the antiaromaticity of compound (I), which contains an annelated cyclobutadiene fragment. The energy of the antiaromatic destabilisation of CBD after taking into account the influence of steric effects in the system of compound (I) (see also Herr[137]) has been estimated as 60–80 kJ mol^{-1}.

Another approach[138] is based on a comparison of the activation barriers to the topomerisation reactions (V) ⇌ (VI) and (VII) (VIII) determined by dynamic NMR.



(18)



(19)

The differences between these barriers are attributed to the formation in the first case of the destabilised structure (Va) containing the antiaromatic CBD ring. The resonance energy of the unsubstituted CBD has been estimated as approximately 88 kJ mol^{-1}.

As mentioned above in Section (I), calculations of the heat of the isodesmic reaction (6) also indicate the antiaromaticity of CBD.

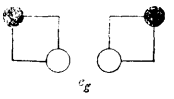
Paramagnetic ring currents have been observed[135] in an NMR study of tri-t-butylcyclobutadiene, which makes it possible to classify CBD as a paratropic system and, in conformity with the magnetic criteria, as an antiaromatic system.

(a) The geometrical structure of the type of the electronic ground state of CBD. The problems of the geometry and the multiplicity of the electronic ground state of CBD have found a reliable theoretical and experimental solution only recently (see the detailed review of Bally and Masamune[135]). Here we shall note only the most significant features.

Numerous calculations for CBD have led to three possible types of cross-sections through the potential energy surface for the C_4H_4 system corresponding to the locus of the minimum energy of the reaction involving the topomerisation of the CBD structure with D_{2h} symmetry via a structure having the D_{4h} symmetry (Fig.3).

The results of the majority of the calculations show that in the singlet ground state CBD has an equilibrium configuration with D_{2h} symmetry. The scheme in Fig. 3*a* corresponds to the results of Allinger et al.[139] (PPP method, the σ-skeleton is treated by the method of molecular mechanics). On the other hand, the conclusions concerning the energy of the lowest singlet and triplet states having a structure with D_{4h} symmetry have been contradictory. For the CBD structure having this symmetry, two electrons in the e_g orbitals can be accommodated in different ways, which leads to six degenerate configurations within the framework of the one-determinant approximation.

By considering their interactions and using the symmetry properties, it can be shown that in the given instance there is a possibility of the electronic states $^1A_{1g}$, $^1B_{1g}$, $^1B_{2g}$ and $^3A_{2g}$ (whose energies relative to that of the $^3A_{2g}$ state are 280, 251, and 29 kJ mol^{-1} according to the results of non-empirical calculations in terms of the 6-31G basis set[89]), differing in the ways the electrons are accommodated in the orbitals. Orbitals of the e_g type are localised at different carbon atoms:



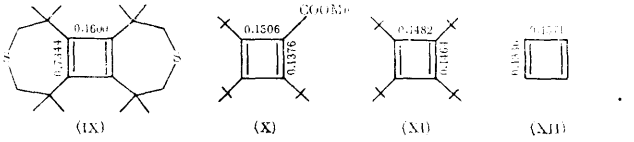
The corresponding exchange integral should be very small (it should be approximately zero in terms of the NDO approximation), which has two consequences. Firstly the energies of the $^3A_{2g}$ and $^1B_{1g}$ states are similar, because the electrons in the e_g orbitals are separated in space and the energy of the interelectron interaction depends less on whether the spins are parallel of not.[90] Secondly, as a result of the dynamic spin polarisation#, which is much more effective in the case of the singlet state, the energy of the $^1B_{1g}$ state is lower than that of the $^3A_{2g}$ state (see the scheme in Fig. 3*c*). Since this type of effect cannot be described in terms of the approximation of the RHF method without taking into account the configuration interaction, the energy of the $^1B_{1g}$ state is significantly too high.

The electronic structure of CBD with a nuclear configuration having the D_{4h} symmetry cannot be described satisfactorily in terms of the one-determinant approximation and, for example, non-empirical calculations in terms of the 4-31G basis set lead to the conclusion that the triple state of the CBD molecule with D_{4h} symmetry has an energy lower by 22.6 kJ mol^{-1} than that of the singlet state with a nuclear configuration with D_{2h} symmetry (Scheme *a* in Fig. 3).[141]

Non-empirical calculations with allowance for configuration interaction lead to differences between the energies of the $^3A_{2g}$ and $^1B_{1g}$ states of 30.5–58.2 kJ mol^{-1} depending on the basis set,[68–90] which confirms the results of the earlier study[142] (1968) which lead to the scheme in Fig. 3*c*. Analogous results have been obtained by the MC SCF calculations for CBD in the π-electron approximation,[143] and also by calculations based on the MNDOC method[144] (the corresponding energy differences are 29.7 and 39.3 kJ mol^{-1}).

The results of the calculations have been confirmed recently by experimental data. Using the technique of flash photolysis, it has been established that the T_1 state of the peralkylated CBD has an energy higher by 50 kJ mol^{-1} than that of the singlet ground state.[145]

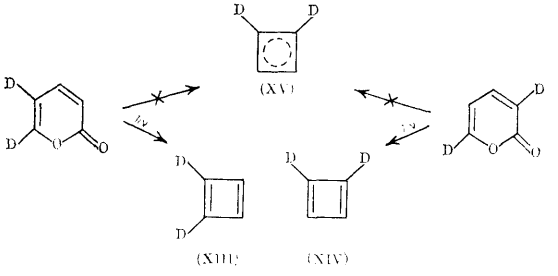
The most accurate calculated data for the geometry of CBD have been obtained by a non-empirical method in a study[67] employing an extended basis set including polarisation functions taking into account the electron correlation (see also, Clark and Harrison[146]). In the singlet ground state of CBD, the carbon σ-skeleton has the form of a rectangle with localised double bonds. It is striking that the C–C bond lengths actually exceed the usual values (the C–C bond length in ethane is 0.1537 nm) which can be accounted for by a tendency towards the decrease of the destabilising effect of conjugation [the results of *ab initio* calculations are quoted for structure (XII) [69]]:



(IX) (X) (XI) (XII)

The considerable differences in the C–C bond lengths are confirmed by the results of X-ray diffraction studies on CBD derivatives of the type of (IX)–(XI).[145,147–149] The equalisation of bond lengths in structure (XI) can be explained by steric causes.[150]

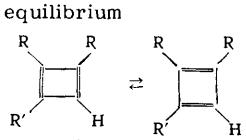
Although the results of earlier investigations[151,152] of the infrared spectra of CBD (isolated in matrices) were interpreted as evidence for a square configuration of the carbon skeleton of the molecule, it was shown subsequently that the presence in the IR spectrum of CBD of four bands due to the skeletal vibrations of the four-membered ring with frequencies below 2000 cm^{-1} [153] can be compatible only with a rectangular molecular structure. This conclusion was recently confirmed by experiments on the matrix isolation of two dideutero-substituted CBD derivatives (XIII) and (XIV) obtained by the photolysis of [5,6-D_2]- and [3,6-D_2]-α-pyrones respectively:[154]



(XV) (XIII) (XIV)

Earlier, it has been assumed erroneously that the reactions indicated lead to the formation of the same product having the square structure (XV). Calculation of the IR spectra of 1,2-dideuteriocyclobutadienes confirmed structures (XIII) and (XIV).[155]

The study of the equilibrium



(20)

R = t-C_4H_9, R′ = 1) t-C_4H_9, 2) t-C_4D_9

#Its essential feature is as follows.[140] The e_g orbitals are localised at different carbon atoms and the electrons present in them, which have opposed spins in the case of a singlet state, determine the disposition in space of the remaining electrons in the preceding, in terms of energy, CBD orbitals, since the repulsion between an electron in one of the e_g orbitals (for example with a spin α) and the electron in the preceding MO with the same spin is smaller, as a consequence of the exchange interaction, than the repulsion between the electrons with the opposite spins. Since the two electrons in the e_g orbital and their spin states are interchangeable, the spin polarisation is dynamic, in contrast to the similar statistical spin polarisation in radicals.

by dynamic ^{13}C NMR provided direct evidence for the existence of the valence isomers of CBD with alternating carbon–carbon bond lengths (in the ring), in contrast to the description of CBD in terms of resonance structures (cf. Fig.2).

Thus, whereas in the case of aromatic compounds, for example, benzene, structures with alternating bond lengths (the structures with $D_{3}h$ symmetry in Fig.2) cannot be observed experimentally, because the transition via the fully symmetrical $D_{6}h$ form does not involve the overcoming of an energy barrier and takes place at an electron oscillation frequency of approximately 10^{15} s^{-1},[152] in the case of CBD reaction (14) does in fact require the movement of nuclei. Thus in the ground state the geometry of CBD belongs to the $D_{2}h$ symmetry group with localised double bonds in the ring. Consequently both the structural criteria of aromaticity–antiaromaticity and the energetic (resonance energies, heats of isodesmic reactions) and magnetic criteria show that CBD is antiaromatic.

(b) Valence isomerisations of CBD. The closeness of the potential energy surfaces for the ground and lowest excited states of antiaromatic compounds leads to the possibility of low-barrier valence isomerisation reactions, in contrast to benzene and other aromatic molecules. Fig.4 illustrates schematically the valence isomerisation reactions of CBD based on calculations by the MINDO/3 method.[157–160]

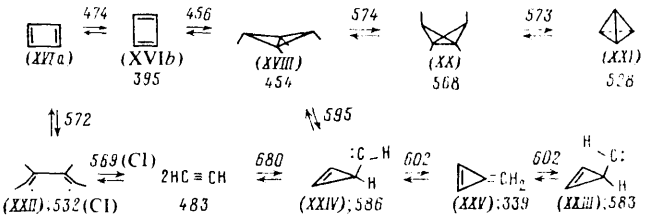
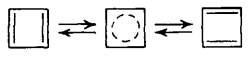
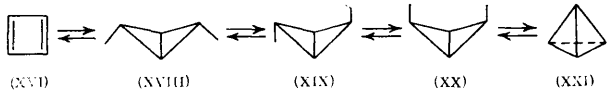


Figure 4. Schemes illustrating the principal valence isomerisations of CBD according to calculations by the MINDO/3 method.[157–160] The numerals under the numbers designating the structures represent the calculated heats of formation (in kJ mol^{-1}) and the numbers along the arrows represent the heats of formation of the structures of the transition state (in kJ mol^{-1}). The calculations for the cyclodimerisation of acetylene to CBD have been made taking into account the configuration interaction (CI).[159] The concerted cyclisation mechanism cannot be described satisfactorily within the framework of the one-determinant approximation because of the triplet instability of the RHF solutions.[160]

Two types of reactions are possible theoretically in principle: topomerisation occurring as a fluctuation of π-bonds in the ring [the bond shift process—see Eqn.(14)],



and the interconversion of CBD and the only theoretically permissible isomeric form—tetrahedrane:



(21)

The isomerisation reaction (14) can be regarded as the manifestation of a second-order Jahn–Teller effect. The lowest singlet $^{1}B_{1g}$ state of the structure with $D_{4}h$ symmetry can be mixed with the $^{1}A_{1g}$ state, which has a similar energy, as a result of vibrations with $b_{1}g$ symmetry corresponding to deformations which convert the CBD structure with $D_{4}h$ symmetry into the rectangular form.[89] The triplet $^{3}A_{2}g$ state of the $D_{4}h$ structure of CBD might be mixed, as a consequence of the $b_{1}g$ vibration, with the $^{3}B_{2}g$ state, but the triplet state with a suitable symmetry has an unduly high energy. This in fact explains why the geometry with $D_{4}h$ symmetry corresponds to the $^{1}A_{2}g$ state of CBD.

It has been suggested[161] that the interconversion of the rectangular $D_{2}h$ topomers of CBD of the type of compounds (XVIa) and (XVIb) (Fig.4) can proceed via a rhombic and not quadratic transition state with $D_{2}d$ symmetry. However, in the case of the CBD structure having the $D_{4}h$ symmetry there are no excited singlet states whose interactions with the $^{1}B_{1}g$ state would lead to the rhombic distortion of the structure.[88,89]

It follows from the results of non-empirical calculations that the $^{1}B_{1}g$ state with a $D_{2}h$ structure of CBD has only one negative force constant corresponding to the $b_{1}g$ distortion, while the $^{1}A_{2}g$ state has no negative force constants. Thus the $D_{2}h$ structure of CBD in the $^{1}B_{1}g$ electronic state does indeed correspond to the transition state in the topomerisation of the $D_{2}h$ structure and the activation barrier has been estimated as 34.7–56.1 kJ mol^{-1} (*ab initio* calculations[88–90]).

We may note that Dewar and Kollmer[157] quote an energy difference between the lowest singlet and triplet states of the CBD structure with $D_{2}h$ symmetry amounting to 54.8 kJ mol^{-1} (MINDO/3 method). Correspondingly, the activation barrier to the topomerisation of $D_{2}h$ structures is 79.5 kJ mol^{-1}, but, in terms of the NDO approximation, the above energy difference between the lowest singlet and triplet states should be zero. Indeed the calculations for the CBD molecule by the MINDO/3 method, which we repeated, confirmed this. The activation barrier to the topomerisation of the $D_{2}h$ structures of CBD proved to be 24.7 kJ mol^{-1}, which agrees well with the results of non-empirical calculations,[88–90] in contrast to the results of Dewar and Kollmar.[157] The use by the latter workers of an initial density matrix corresponding to the double filling of one of the CBD molecular π-orbitals with e_{g} symmetry led to an artefact solution.[125] This is yet another example demonstrating the complexity of the calculation of the electronic structure of antiaromatic molecules discussed above (Section I).

The experimental barrier to the topomerisation of tri-t-butylcyclobutadiene found by dynamic NMR is 10.5 kJ mol^{-1}.[162]

The direct thermal cyclisation of CBD to tetrahedrane [reaction (21): ($\pi 2a + \pi 2a$ – cycloaddition)] and the reverse reaction are forbidden by the Woodward–Hoffman rules,[163] which is the reason for the kinetic stability of tetrahedrane, whose energy is higher than that of CBD.[69,146,164–169] Indeed, the valence isomerisation of tetra-t-butyltetrahedrane to tetra-t-butylcyclobutadiene takes place only at 135 °C and above.[170,171] The reversibility of the isomerisation has been confirmed by low-temperature NMR data. In view of the prohibition of the concerted mechanism of the thermal isomerisation CBD ⇌ tetrahedrane, reaction (21) has been shown by calculations[69,166–168] to proceed in several stages involving the formation of the diradicaloid intermediates (XVIII) and (XX) (Fig.5).

The following values have been obtained for the total activation energy for the isomerisation reaction CBD → tetrahedrane: 179.5 kJ mol^{-1} (MINDO/3 [159]), 255.6 kJ mol^{-1} (MNDO – CI 2 × 2 [168]), and 143.4 kJ mol^{-1} (*ab initio*, DZ + P basis, with allowance for electronic correlation[69]). The diyl (XIX) is the transition state in the reaction (XVIII) → (XX),

which constitutes the rate-limiting stage. The activation barrier for this reaction has been estimated as 142 kJ mol^{-1} (*ab initio*, DZ + P basis, with allowance for correlation energy[69]), 120.9 kJ mol^{-1} (MINDO/3), or 125.1 kJ mol^{-1} (MINDO/3, with allowance for CI 3 × 3 [153]).

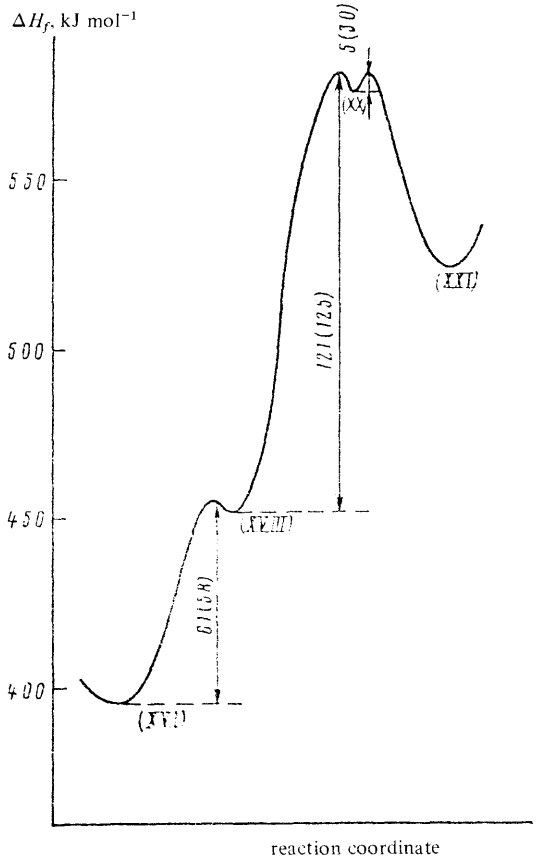
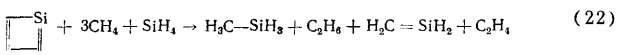


Figure 5. Cross-sections through the potential energy surface for the C_4H_4 structure along the locus of the minimum energy of the reaction involving the CBD → tetrahedrane isomerisation (calculation by the MINDO/3 method[153]). The activation barriers (in kJ mol^{-1}), calculated taking into account the 3 × 3 configuration interaction, are indicated in brackets.

2. Hetero-substituted Cyclobutadienes

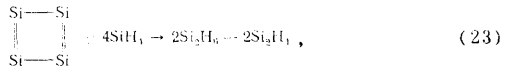
The analogues of cyclobutadiene have been studied to an incomparably lesser extent than cyclobutadiene itself. Calculations and individual experimental data are available only for sila- and aza-substituted derivatives.

Silacyclobutadiene. The results of the calculation of the heat of the isodesmic reaction (22) (*ab initio*, 6-31G/3-21G basis[61])



(22)

(ΔH = −223 kJ mol^{-1}), which is a characteristic of the stability of the conjugated cyclic system, indicate the antiaromaticity of silacyclobutadiene. On this scale, the degree of antiaromaticity of cyclobutadiene exceeds by 61.1 kJ mol^{-1} that of silacyclobutadiene [see reaction (6)]. This is caused mainly by the fact that the introduction of the silicon atom with its diffuse atomic orbitals into the ring decreases the destabilising effect of the conjugation in the four-membered ring. Indeed the degree of antiaromaticity of tetrasilacyclobutadiene, estimated from the heat of reaction (23) by the MINDO/3 method, is significantly lower than in the case of cyclobutadiene:[172]

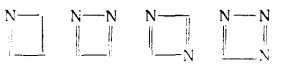


(23)

for which ΔH = −68.6 kJ mol^{-1}.

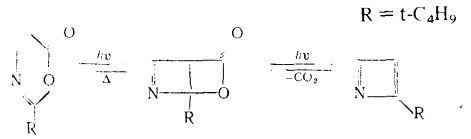
According to the results of non-empirical calculations (6-31G/3-21G basis),[61] silatetrahedrane has a total energy higher by 139.3 kJ mol^{-1} than silacyclobutadiene.

Azacyclobutadienes. The unsubstituted azacyclobutadiene (azet) (XXVI) has not so far been obtained, but there exist data demonstrating the experimental detection of a number of its derivatives.[173,174]



(XXVI) (XXVII) (XXVIII) (XXIX)

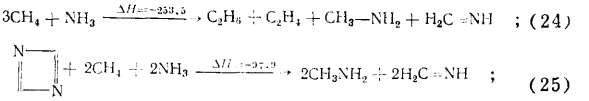
For example, when oxazinone was irradiated, t-butylazacyclobutadiene was obtained:



In order to compare the properties of cyclobutadiene and its aza-derivatives, we shall discuss the influence of aza-substitution on the e_g π orbitals of CBD with D_{4h} symmetry (Fig. 6).

Monoaza-substitution leads to the removal of degeneracy from the e_g π orbital in the D_{4h} structure of CBD, stabilising the a_1 π orbital (the C_{2v} structure of azet)[54] (the change in the energies of the π orbitals of conjugated cyclic systems on aza substitution has been considered;[176] see also the aza-substitution of trimethylenemethane in the case of Y-antiaromaticity[177]). 1,3-Diaza-substitution leads to an even greater change in the relative energies of the e_g π orbitals, stabilising the b_{2g} orbital. This results in an increase of the energy difference between the ground ^1A_g and the first excited singlet $^1B_{1g}$ states of the structure of 1,3-diazet with D_{2h} symmetry, which promotes an increase of both the antiaromatic character and the lattice instability of the structure in conformity with the aromaticity-antiaromaticity criteria.[16,81] 1,2-Diaza-substitution should not lead to an appreciable stabilisation of any one of the e_g π orbitals of the D_{4h} structure of CBD relative to another.

Calculations by the MINDO/3 method of the heats of the isodesmic reactions (24)–(26) indicate a higher stability of 1,3-diazet compared with 1,2-diazet and of azet compared with cyclobutadiene[59] (the values of ΔH for the reaction are indicated in kJ mol^{-1}):



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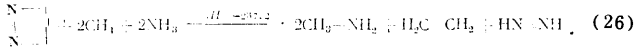


(26)

The results of non-empirical calculations (STO-3G basis) of the heats of reaction (25) also indicate a greater stability of 1,3-diazet ($\Delta H = -201.4$ kJ mol^{-1}) compared with CBD ($\Delta H = -268.6$ kJ mol^{-1}).[60]

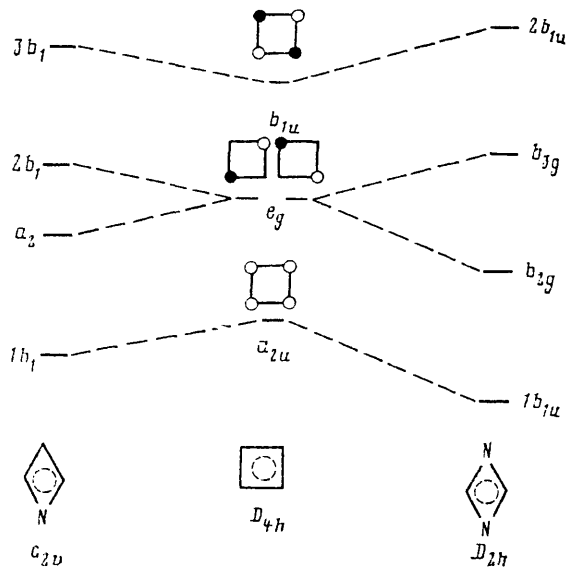


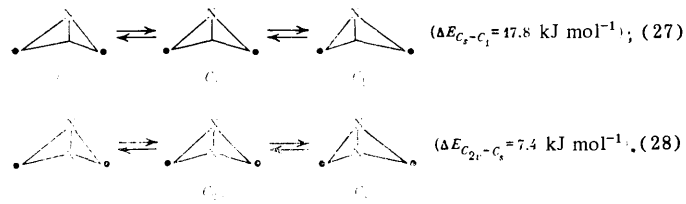
Figure 6. Correlation of the π MO for the cyclobutadiene structure, the azet structure with D_{2h} symmetry, and the 1,3-diazet structure with D_{2h} symmetry.

A decrease of the antiaromatic character of azet compared with CBD follows from the calculations of the Dewar resonance energy: −71.1 kJ mol^{-1} [44] and −64.8 kJ mol^{-1} [178] have been obtained for CBD and azet respectively. Despite the variation of the initial density matrix, calculations by the Pariser–Parr–Pople (PPP) method for 1,2-diazet cannot yield a solution corresponding to a structure with equalised bond lengths.[179,180]

The substitution of three carbon atoms must be treated as a special case because in this instance both e_g π orbitals of the CBD structure with D_{4h} symmetry are stabilised. The structure with alternating bond lengths having the C_S symmetry corresponds to a minimum on the potential energy surface for CN_3H and not the structure of triazet with C_{2v} symmetry (calculations by the MINDO/3 method[59]). Consequently, in contrast to the tendencies characteristic of mono- and 1,3-di-aza-substitution, 1,2-diaza-substitution and triaza-substitution do not stabilise the highly symmetrical configuration, which, by virtue of the small energy difference between the ground and first excited singlet states, involves lattice instability.[179,180]

Thus analysis of the transformations of the molecular orbitals of the CBD molecule with D_{4h} symmetry for different types of aza-substitution justifies the expectation of three different types of potential energy surface corresponding to reactions (14) and (21) for azacyclobutadienes. (The results of the calculations and of the valence isomerisations of azacyclobutadienes are presented in Fig.7).

Isomerisation to structures of lower symmetry is characteristic of the C_S structure of 1-azabicyclo[1.1.0]butane-2,4-diyl (XXXI) and the C_{2v} structure of 1,3-diazabicyclo[1.1.0]-butane-2,4-diyl (XXXVII) [59] (the energy differences calculated by the MINDO/3 method are indicated in brackets):



($\Delta E_{C_2-C_1} = 17.8$ kJ mol^{-1}); (27)

($\Delta E_{C_{2v}-C_s} = 7.4$ kJ mol^{-1}). (28)

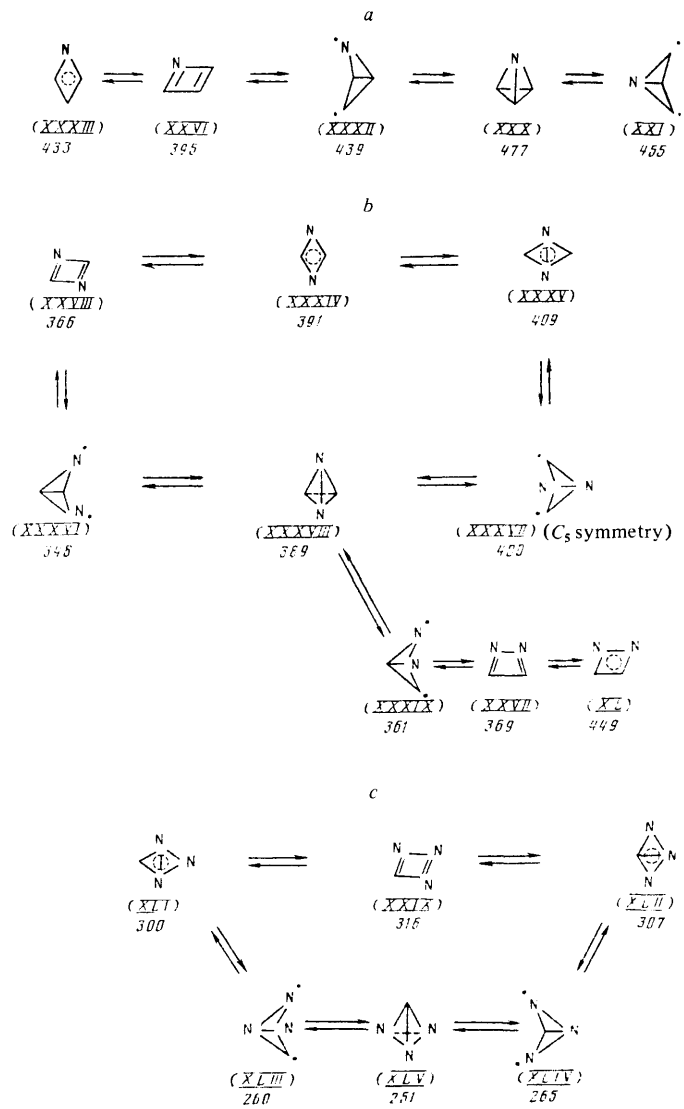


Figure 7. Schemes illustrating the valence isomerisations of azet (*a*), 1, 2- and 1,3-diazets (*b*), and triazet (*c*). The numerals under the numbers designating the structures represent the heats of formation (in kJ mol^{-1}) calculated by the MINDO/3 method.[59,179,181] Minima on the potential energy surface correspond to all the structures with the exception of structures (XXXIII), (XXXIV), and (XL), to which maxima correspond.

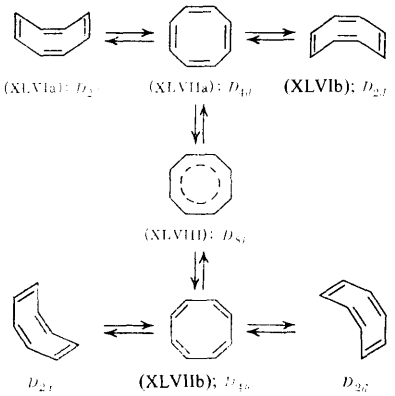
The reactions involving the cyclisation of azabicyclo[1.1.0]-butanediyls to the corresponding azatetrahedranes are prohibited by bond symmetry conservation rules[182] (see Glukhovtsev et al.[59] for the given reactions) and are characterised by high activation barriers, which is the reason for the kinetic stability of the corresponding azatetrahedranes.

3. Cyclo-octatetraene

The structure of cyclo-octatetraene (COT), which is the second member of the series of [4*n*]annulenes with $n = 2$, has been studied in extremely great detail.[183–185] This compound and some of its derivatives are stable substances and there exist fairly reliable experimental data for their geometry, the type of the electronic ground state, and the most characteristic chemical properties.

The boat configuration (XLVI) with D_{2d} symmetry corresponds to the COT molecule in the ground state. According to calculated data,[186–188] its energy is lower by 63–75 kJ mol^{-1} than that of the planar structure (XLVII) with D_{4h} symmetry. Only one compound with a planar cyclo-octatetraene fragment is known, namely the cyclic perfluorotetracyclobutane derivative, in which there is a slight alternation of the bond lengths in the COT ring (0.1425 nm) according to X-ray diffraction data.[189]

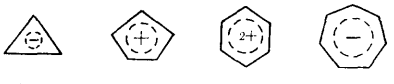
The planar forms of COT with D_{4h} and D_{8h} symmetries are the transition states for the most important COT isomerisation reactions—the enantiomerisation (XLVIa) ⇌ (XLVIb) and the structural topomerisation (XLVIIa) ⇌ (XLVIIb) respectively. The latter process is isotypical with the topomerisation of the D_{2h} structure of CBD.



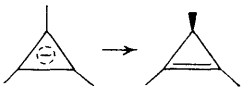
In the case of certain tri- and tetra-methyl-substituted COT the isomerisation, involving the formation of structure (XLVIII) with D_{8h} symmetry (fluctuation of π-bonds), can compete with the ring inversion which proceeds via the D_{4h} structure, although the barrier to ring inversion in COT is lower by 8.4–12.5 kJ mol^{-1} (see the relevant reviews[78–84]). Comparison of the activation energies for ring inversion and for the fluctuation of π-bonds makes it possible to estimate the COT delocalisation energy. The difference between these energies was found to be 14.2 kJ mol^{-1} in the case of 1,3-di-t-butylcyclo-octatetraene.[78] The antiaromatic character of COT is thus fairly weak.[77]

4. Antiaromatic Monocyclic Ions

The cyclic ions (XLIX)–(LII) containing $4n$ π-electrons and having a ring symmetry D_{mh} ($m = 3$, 5, 6, and 7 respectively) have an unclosed electron shell. In the singlet state in such systems a second-order Jahn–Teller effect is observed, being manifested, as in the case of CBD and COT, by a transition to a geometrical structure with a reduced symmetry and involving alternating bond lengths.

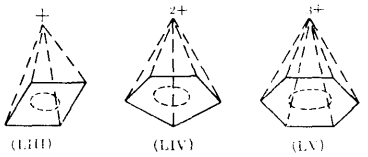


There is also a possibility of the formation of non-planar systems, which leads to the breakdown of cyclic conjugation as a result of the exclusion of one of the p_z orbitals from the conjugation system and to a decrease of the degree of antiaromaticity of the molecule, for example, in the case of the cyclopropenyl anion (CPA):

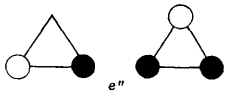


(29)

In addition the ions (L)–(LII) can have isomers in the form of non-classical polyhedral structures with $C_{(m-1)}$ symmetry provided that the latter satisfy the essential electronic requirements for three-dimensional aromaticity,[28] for example:



The cyclopropenyl anion. The unsubstituted CPA has not so far been obtained, but is triphenyl derivative is known. It has a strongly antiaromatic character, which is confirmed by the unusually high pK_a of its conjugate acid—triphenylcyclopropene (p$K_a \geq 51$).[9,20] Calculations[190–194] show that CPA has a triplet ground state and the D_{3h} geometry. Since the π orbitals with e'' symmetry cannot be localised in such a way that they have no common carbon atom, the corresponding exchange integral is fairly high.



As a result, the dynamic spin polarisation is not any way significant, in contrast to CBD and Hund's rule holds.[140]

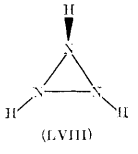
The degenerate character of the highest incompletely occupied e'' orbitals in the CPA structure with D_{3h} symmetry [the π-electron configuration of the state is $(a_2'')^2(e'')^2$] leads, as for CBD, to a second-order Jahn–Teller effect and to a decrease of the energy of the singlet $^1A_1$ state§ by 48.9 kJ mol^{-1} as a result of the decrease of the symmetry of the nuclear configuration to C_{2v} [194] [structures (LVIIa) and (LVIIb) with unequal C–C bond lengths]:

§ The designations for the electronic states of CPA and the cyclopentadienyl cation (CPC) correspond to the C_{2v} symmetry group (for further details, see the relevant literature[29,194–196].

The energies of the C_{2v} structures (LVIIa) and (LVIIb) (in kJ mol^{-1}) are indicated in brackets relative to the energy of the $^3A'_2$ state of the D_{3h} structure (LVI), found by a non-empirical method (STO-3G, CI basis);[194] the numerals opposite the bonds represent their lengths in nm.

However, in contrast to CBD, the singlet $^1A_1$ state is not the electronic ground state of CPA. This important conclusion must nevertheless be regarded as preliminary, because sufficiently reliable results can be obtained only by calculations where account is taken of the interaction of the configurations constructed not only on the basis of π orbitals but also σ orbitals.[195,196] Indeed, calculations carried out taking into account the configurations constructed on the basis of π orbitals describe incorrectly the form of the potential energy surface for the $^1A_1$ state.[196]

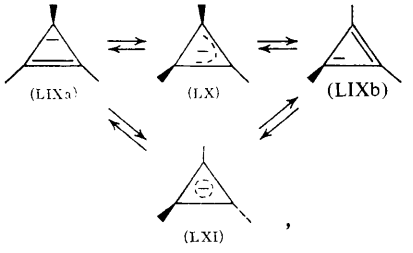
Non-empirical calculations[190] and calculations performed by the MINDO/3 and NDDO [193] methods have shown that additional stabilisation of the singlet state of CPA is achieved as a result of the displacement of the C–H bond in structures (LVIIa) and (LVIIb) from the plane of the three-membered ring. According to the results of non-empirical calculations (taking into account CI) for the $(NH)_3^{2+}$ system,[195] which is isoelectronic with respect to CPA, the electronic triplet state of the planar structure having the D_{3h} symmetry has a lower energy than the singlet state. However, the ground state of the ion $(NH)_3^{2+}$ is of the singlet type and a structure with displacement of the N–H bond from the plane of the ring in (LVIII) corresponds to it:



(LVIII)

The energy of the triplet state is also reduced in a structure of this type but to a lesser extent than that of the singlet state.

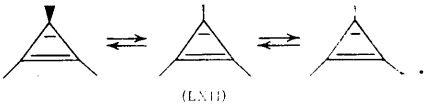
The valence isomerisations of CPA. The high symmetry (D_{3h}) of the CPA structures subjected to the Jahn–Teller effect is responsible for the formation of a multiplicity of local minima on the potential surface in the vicinity of the point corresponding to the given structure. According to the Murrell–Laidler theorem,[197] the singlet state of the structure with D_{3h} symmetry cannot be the transition state for the isomerisations of configurations having a lower symmetry, which has been confirmed by calculations.[192,194] Two types of isomerisations are possible, namely fluctuations in the position of the double bond [structures (LX) and (LXI) are the transition states]:



(LIXa) (LX) (LIXb) (30a)

(LXI) (30b)

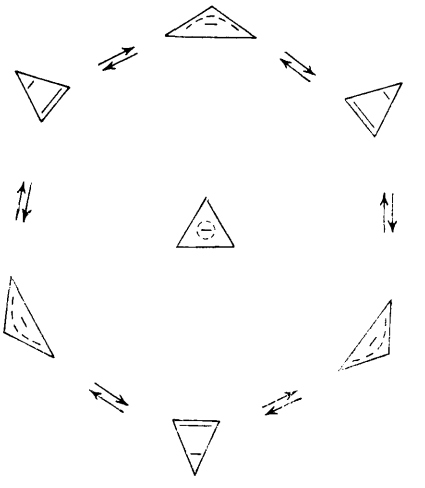
and the inversion of the carbanionic carbon [structure (LXII) is the transition state]:



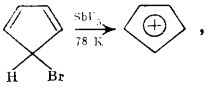
(LXII) (31)

The activation energies for reactions (30a) and (31) calculated by the CNDO/2 method[92] are 90 and 107 kJ mol^{-1}. An activation energy of 88.7 kJ mol^{-1} corresponds to the isomerisation reaction (30b), which proceeds via the transition state (LXI).[192]

The fluctuation of the double bond in planar structures (singlet state) of CPA of the type (LVIIa) and (LVIIb) can be represented by the following scheme, which shows that the reaction pathway runs in the "valley" encircling the "top of the hill" on the potential energy surface corresponding to the configuration with the D_{3h} symmetry:

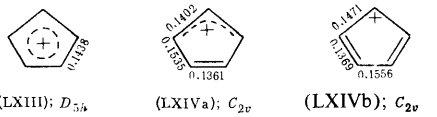


The cyclopentadienyl cation (CPC). Experimental studies, especially the EPR spectrum of CPC obtained by treating 5-bromocyclopentadiene with antimony pentafluoride at 78 K,[198]



(32)

confirmed the results of quantum-chemical calculations[199–204] showing that the electronic ground state of CPC (LXIII) is of a triplet type and has a geometry with D_{5h} symmetry. The energy of the singlet state corresponding to structure (LXIV) with C_{2v} symmetry is higher by only 30.5 kJ mol^{-1} (*ab initio* calculation, STO-3G, CI basis[204]).

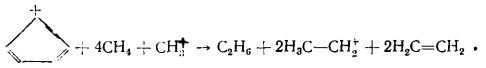


(LXIII); D_{5h} (LXIVa); C_{2v} (LXIVb); C_{2v}

The comparatively small difference between the energies of the singlet and ground states makes it possible to stabilise the former by introducing substituents into the ring.[205] In the case of the $^1A_1$ state of the structure with D_{5h} symmetry a second-order Jahn–Teller effect is observed.[29,204] The stabilisation energy on transition to the structure with C_{2v} symmetry is 56.1 kJ mol^{-1},[201] which is approximately three times greater than the analogous quantity calculated on the basis of the same scheme for CBD.[29] This can be accounted for by the greater similarity of the energies of the states, which can become mixed on distortion of the geometry of the nuclear skeleton of the CPC.

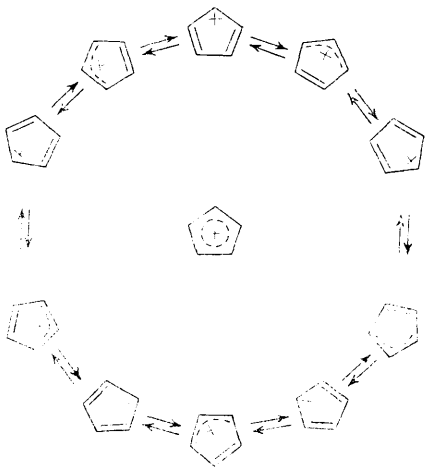
The antiaromaticity of CPC is confirmed both by the alternation of the bond lengths in structures of the singlet state and by the resonance energies (Table 1) and the heat of the

isodesmic reaction (33), which amounts to −12.6 kJ mol^{-1} (*ab initio* calculation, 4-31G basis).[202]

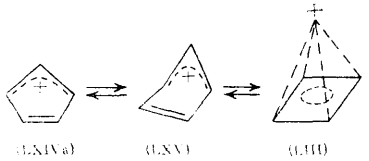


(33)

The valence isomerisations of CPC. Two main types of valence isomerisation are possible for CPC—the shift of the π-bonds in the planar structure described as pseudorotation of structures with C_{2v} symmetry:



and isomerisation to the classical square pyramidal structure (LIII), the possibility of the existence of which has been demonstrated by calculations using the extended Hückel method (EHM):[206]



(LXIVa) (LXV) (LIII) (34)

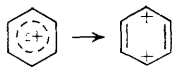
The pathway of the reaction involving bond shifts does not intersect the region corresponding to the D_{5h} configuration, which cannot be the transition state in the given reaction according to the Murrell–Laidler theorem.[197] Indeed, calculations have shown[204] that the symmetry-prohibited concerted isomerisation reaction $C_{2v} \rightarrow D_{5h} \rightarrow C_{2v}$ has a considerable activation barrier. The minimum energies for structures (LXIVa) and (LXIVb) differ by not more than 4.18 kJ mol^{-1}.[204]

The activation barrier of reaction (34) involving isomerisation to the square pyramidal structure (LIII), having an energy higher by 58.6 kJ mol^{-1} than structure (LXV), is 238.6 kJ mol^{-1} (MINDO/3 method[200]). According to revised data,[203,207] structure (LXV) is in its turn more stable by only 2.9 kJ mol^{-1} than structure (LXIVa). An interconversion reaction, whose transition state is structure (LXVI), is possible for structure (LIII), the activation barrier amounting to 77.8 kJ mol^{-1} (calculation by the MINDO/3 method).[39]

(LXVI)

The existence of structure (LIII) has been confirmed experimentally (the dimethyl derivatives[208] and also the trimethyl derivative[209] have been obtained; see also the relevant reviews[210,211]).

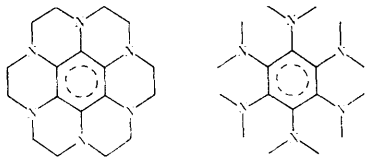
The benzene dication. The studies on the benzene dication and its fragmentation pathways have been the subject of numerous investigations.[212–214] Calculations by the MINDO/3 method have shown that the triplet state of the structure with D_{6h} symmetry is more stable by 40 kJ mol^{-1} than the singlet state,[214] which agrees with experimental data indicating a triplet ground state of the hexachlorobenzene dication.[215] When the limitations due to the D_{6h} symmetry were removed in the course of calculations on the structure of the singlet state of the benzene dication (LI), a distortion of the geometry was observed (without an activation barrier), resulting in the conversion into the less symmetrical structure (LXVII) with D_{2h} symmetry, whose energy is lower by ~320 kJ mol^{-1}.[214]



(LI: D_{6h}) (LXVII: D_{2h})

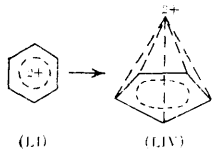
At the same time, structure (LXVII), which has four π electrons, is insufficiently well favoured by energy factors, which leads to the possibility of its fragmentation into acyclic structures.

A number of procedures have been proposed for stabilising the benzene dication by introducing substituents,[216,217] for example, as in systems (LXVIII)–(LXIX).



(LXVIII) (LXIX)

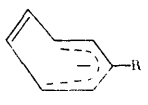
As in the case of CPC, one can assume that the antiaromatic character of the benzene dication promotes its isomerisation to the more stable non-classical pyramidal structure (LIV).



(LI) (LIV)

The hexamethyl derivative of the dication (LIV) is stable under the usual conditions.[218]

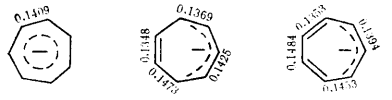
The cycloheptatrienyl anion. It has been suggested that the cycloheptatrienyl anion (CHA) is an intermediate in many reactions,[219,220] including the cycloheptatriene dimerisation reaction under the influence of bases.[221] Certain monosubstituted CHA, investigated by NMR which indicates a non-coplanar structure (LXX), are known.[222]



(LXX)

Here R = CO_2R^1, $CONR^2R^3$, or SO_2R^1, where R^1, R^2, and R^3 are aryl or alkyl. The planar structure of CHA with D_{7h} symmetry (eight π electrons) has a pair of e' orbitals (π4 and π5 orbitals), which are degenerate with respect to energy. In this case there is a possibility of the following electronic states: a triplet ($^3A'_2$) and two singlet ($^1A'_1$ and $^1E'_3$) states. As a consequence of a second-order Jahn–Teller effect, the state E'_3 is mixed with the low-lying singlet state $^1A_1$, which distorts structure (LII) to give structures (LXXI) and (LXXII) with C_{2v} symmetry. Calculations by the MINDO/3

and MNDO methods have shown that minima on the potential energy surface of the $(CH)_7^-$ ion correspond to the planar structures (LXXI) and (LXXII) having similar energies [the numerals under the numbers of the structures represent the energies relative to structure (LXXI) in kJ mol^{-1} found by the MINDO/3 method; the numerals in brackets have been found by the MNDO method;[222] the numbers opposite the bonds represent their length in nm calculated by the MINDO/3 method]:

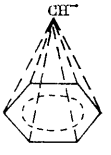


(LII); D_{7h} 30.6 (27.2) (LXXI); C_{2v} 0 (0) (LXXII): C_{2v} 0.04 (0.17) .

These results can be regarded as preliminary in view of the known tendency of the MINDO/3 and MNDO methods to "flatten" cyclic hydrocarbon structures.[223]

The energy of the triplet state of the structure with D_{7h} symmetry is higher by 9.8 kJ mol^{-1} than that of the singlet state of structure (LXXI) with C_{2v} symmetry (the MINDO/3 method).[222]

Isomerisation involving bond shifts may be expected for CHA, i.e. (LXXI) → (LXXII), which is analogous to that examined above for the cyclopentadienyl cation. The isomerisation to the pyramidal structure (LXXIII)

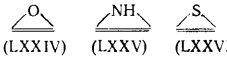


(LXXIII): C_{6v}

does not occur in this case because the electron count rules[39] do not hold for structure (LXXIII) and such a system must be unstable.

5. 4π-Electron Three-membered Heterocycles

Oxiren (LXXIV), 1H azirine (LXXV), and thi-iren (LXXVI) are known as extremely unstable compounds, which can be isolated only using the matrix isolation technique (see the review of Tores et al.[224]).



(LXXIV) (LXXV) (LXXVI)

Oxiren and its substituted derivatives have been proposed as intermediates in many reactions, in particular in the Wolff rearrangement of α-diazoketones. However, the experimental attempt to identify oxiren as an intermediate in this reaction were unsuccessful.[225] Indeed quantum-chemical calculations, including non-empirical calculations with allowance for electron correlation, have shown that a very shallow minimum on the potential energy surface of the C_2H_2O system corresponds to oxiren. Furthermore, oxiren has a much higher energy than isomers such as, for example, keten and hydroxyacetylene.[193, 226–233] The kientic stability of oxiren is extremely low. Thus the activation barrier to the isomerisation to formylmethylene has been estimated as only 3.3 kJ mol^{-1} (*ab initio* calculation, DZ + P basis, allowance for electron correlation),[230] while that for isomerisation to keten is about 32 kJ mol^{-1}.[231] Such instability of oxiren can be accounted for by the fact that in the series of systems (LXXIV)–(LXXVI) the mechanism of the reverse $p \rightarrow \pi^*$ donation, which stabilises the three-membered ring, is least evident for oxiren by virtue of the greater electronegativity of oxygen.[39]

III. NON-ALTERNANT[*n*]ANNULENO[*n*]ANNULENES CONTAINING INTERNAL OR PERIMETRIC 4*m*π-ELECTRON RINGS

The question of the aromatic or antiaromatic character of compounds of this series, namely propalene (LXXVII), pentalene (LXXVIII), and heptalene (LXXIX), has aroused a prolonged controversy.

(LXXVII) (LXXVIII) (LXXIX)

The Hückel rule has been derived in the study of monocylic systems and its direct application to annulenoannulenes is incorrect (see also Section IV). Calculations by the HMO method yielded similar delocalisation energies for azulene and heptalene.[41,234] However, the conclusion that heptalene is aromatic, based on this finding, conflicts with experimental data indicating the absence of any manifestations of aromatic character by heptalene.[7]

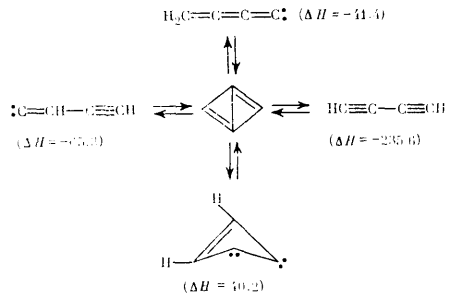
Higher delocalisation energies have also been obtained for pentalene,[7,41] which serve as a basis for the conclusion concerning its stability.[235] At the same time, the unsuccessful attempts to synthesise pentalene (see the relevant reviews[236, 237]) contradict to this conclusion. All these factors stimulated much interest in detailed calculations of the electronic structures of non-alternant [*n*]annuleno-[*n*]annulenes.

1. Propane

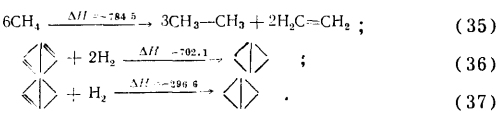
Propalene [bicyclobutadiene (LXXVII)] is stable, according to MINDO/1 calculations, relative to its valence isomer diacetylene, whose photochemical cyclisation is believed to be capable of resulting in the formation of propalene.[238] Calculations by the MINDO/1,[238] MINDO/3,[239] MNDO,[240] and *ab initio* [240] methods indicate a C_2h structure of the ground state, which is more stable than the orthorhombic D_{2h} structure with equalised lengths of the peripheral carbon–carbon bonds in the ring (Table 2). However, according to the results of calculations by the MNDO method,[240] diacetylene has a lower energy than propalene and the activation barrier to the isomerisation of propalene to the carbene (LXXX) has been estimated as only 3.8 kJ mol^{-1}:

(LXXVII); C_{2h} (LXXX) .

Non-empirical calculations in terms of the 4-31G basis altogether failed to demonstrate the existence of a barrier, which, in combination with the data in Table 2, permitted the authors[240] to conclude that propalene is thermodynamically and kinetically unstable in contrast to the optimistic predictions of Baird and Dewar.[238] The relative stability of propalene can be estimated from the calculated heats (the ΔH are indicated in kJ mol^{-1}) of the isomerisation reactions (the MINDO/3 method):[239]



The propalene ring strain energy has been estimated [using the isodesmic reaction (35)] as 784.5 kJ mol^{-1} (the MNDO method).[240] Calculation of the resonance energies by the method of Hess and Schaad indicates the antiaromaticity of propalene,[241] which is greater than that of pentalene (Table 1). At the same time the energy of the antiaromatic destabilisation, determined from the heats of the hydrogenation reactions of propalene [reaction (35)] and 1-bicyclobutene [reaction (36)] has been estimated as only 108.9 kJ mol^{-1}, which is much less than the strain energy (the ΔH for the reactions are indicated in kJ mol^{-1}):



(35)

(36)

(37)

Table 2. The relative energies (in kJ mol^{-1}) of the C_4H_2 valence isomers.

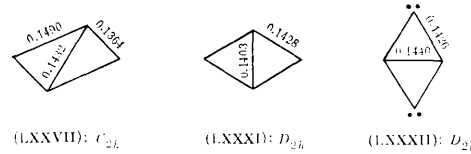
Structure	Method of calculation							
	MINDO/3 (Ref.239)	MNDO (Ref.240)	STO/3G (Ref.239)	4-31G//STO-3G (Ref.239)	4-31G (Ref.240)	MP2[a]/4-31G (Ref.240)	6-31G*//4-31G (Ref.240)	MP2[a]/6-31G* (Ref.240)
(LXXVII)	0	0	0	0	0	0	0	0
(LXXX)	−65.3	−247.3	—	—	−236.4	−123.0	−137.2	−23.8
(LXXXI)	32.2	56.4	63.6	42.7	64.9	—	—	—
(LXXXII)	163.2	—	82.8	87.4	—	—	—	—
(LXXXIII)	38.9	—	−98.7	−28.8	—	—	—	—
(LXXXIV)	211.7	—	128.9	128.4	—	—	—	—
(LXXXV)	−235.6	−536.4	—	—	−421.3	−284.5	−306.3	−269.4

[a] An estimate of the electron correlation energy in terms of the Meller–Plesset perturbation theory taking into account second-order terms.

The minimum on the potential energy surface for the C_4H_2 system does not correspond to the propalene structure with D_{2h} symmetry and the latter is converted via a barrier-free process into a structure with C_{2h} symmetry and alternation of bond lengths.[239,240]

Calculations in terms of the π-electron approximation have led to the conclusion that propalene with the D_{2h} configuration is subject to lattice instability.[242] The employment of the UHF approximation does not result in a qualitative change in the conclusions.[243]

Calculations for propalene by the PPP method revealed a multiplicity of solutions of the Hartree–Fock equations with the initial density matrix varied,[125] which is a characteristic feature of calculations for conjugated systems containing internal or perimetric $4n\pi$-electron rings. Indeed, with the exception of instances of an anomolously distorted geometry,[244] calculation by the PPP method leads to the same solution regardless of the initial density matrix or the initial geometry.[245] For example, for an initial benzene geometry with D_{3h} symmetry, calculation by the PPP method in terms of the Dewar σ,π parametrisation[42] (optimisation of bond lengths) leads to a D_{6h} structure (cf. Fig.2). However, depending on the initial density matrix, three different solutions have been obtained for propalene corresponding to a structure with C_2h symmetry and different bond lengths [structure (LXXVII)], structure (LXXXI) with D_{2h} symmetry [the $(b_{1u})^2(b_{2g})^2$ π-electron configuration], and the D_{2h} structure (LXXXII) of the dicarbene type [the $(b_{1u})^2(b_{3g})^2$ π-electron configuration], i.e. the structural data differ in the order of the frontier MO (Fig.8).



(LXXVII): C_{2h} (LXXXI): D_{2h} (LXXXII): D_{2h}

(The numerals along the bonds represent their lengths in nm.)

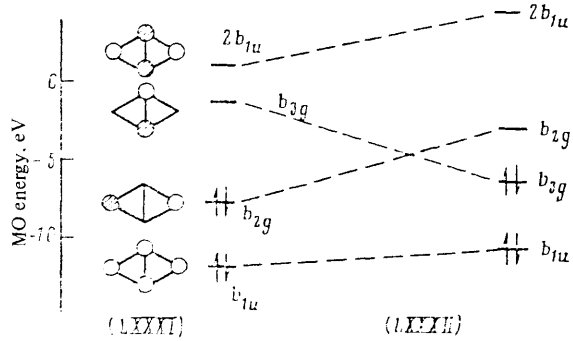
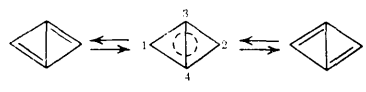


Figure 8. Correlation of the π MO of structures (LXXXI) and (LXXXII) with D_{2h} symmetry (PPP method).[239]

The solution of the Hartree–Fock equations corresponding to structure (XXXII) is unstable with respect to the filling of the MO in order of their increasing energies[107,125,264] (see Section I).

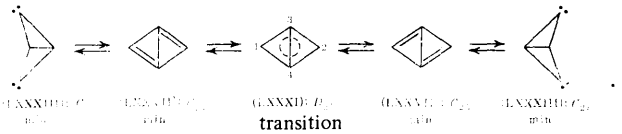
We shall consider the valence isomerisations of propalene. Together with the topomerisation [reaction (38)] of the propalene structure with C_{2h} symmetry, there is a possibility of another non-coplanar mode of isomerisation.



C_{2h} D_{2h} C_{2h} (38)

Indeed, when the length of the transannular bond is altered, the b_{2g} orbital is destabilised, and the b_{3g} orbital is stabilised (Fig.8), there is a possibility of the formation of structure (LXXXII) of the dicarbene type. The instability of the wave function of this structure with respect to the filling of the MO justifies the expectation that propalene can isomerise via the extension of the transannular bond (isomerism involving bond extension[206]). Calculations by the MINDO/3 method confirmed the above hypothesis, as can be seen from the schematic illustration of the valence isomerisation of

propalene (the type of stationary point on the potential energy surface for the C_4H_2 system is indicated under the numbers designating the structures):[239]

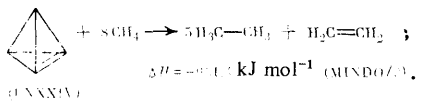


However, the planar structure of the dicarbene type having D_{2h} symmetry, analogous to that obtained in PPP calculations, was converted by a barrier-free process into the non-planar dicarbene structure (LXXXIII) with C_{2v} symmetry.

The relative energies of the valence isomers of C_4H_2, found by semiempirical[239] and non-empirical[240] methods, are presented in Table 2. Evidently, the results obtained in terms of the MINDO/3 approximation are in fact satisfactorily correlated with the results of non-empirical calculations, in which account was taken of the correlation energy by the Meller–Plesset method.

The activation barrier in the isomerisation of propalene (LXXVII) to the non-planar dicarbene C_{2v} structure (LXXXIII) is 72.4 kJ mol^{-1} (MINDO/3) [239] (Fig.9). In contrast to butalene (six π electrons), whose isomerisation on bond extension leads to the formation of *p*-benzyne,[247] the propalene (four π electrons) isomer analogous to 1,3-dehydrocyclobutadiene is not formed. The structure with C_{2v} symmetry, corresponding to the dicarbene structure (LXXXII) found in calculations by the PPP method, is energetically more favourable.

Structures (LXXXIII) can isomerise to dehydrotetrahedrane (LXXXIV), but this compound must be extremely strained:

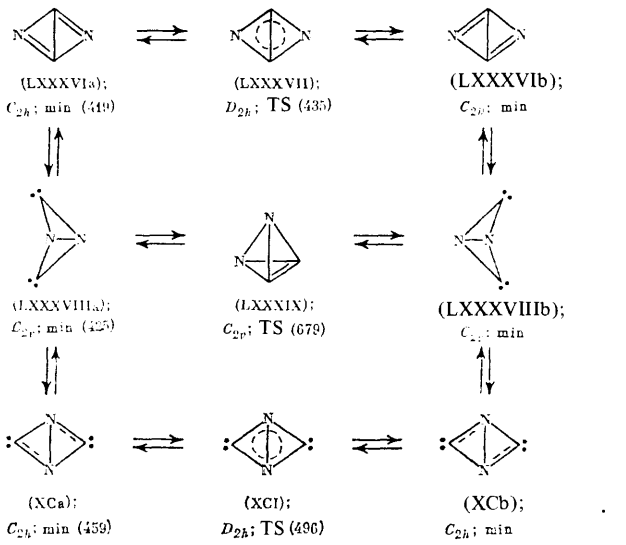


(39)

Analogous data for tetrahedrane (XXI) are presented in the following scheme:

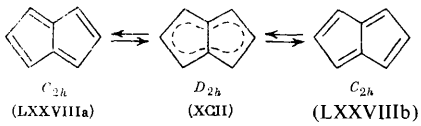
(40)

Diaza-substitution, which stabilises tetrahedrane,[59] does not lead in this instance to the stabilisation of dehydrotetrahedrane, which follows from the results of calculations of the structure of 1,2-diazapropalene and calculations for its valence isomers. Together with the type of symmetry of the structures, the scheme below indicates the character of the stationary point (TS denotes the transition state) on the potential energy surface of the C_2N_2 system, the heats of formation calculated by the MINDO/3 method (in kJ mol^{-1}) being indicated in brackets [we may note that structure (LXXXIX) corresponds, as in the case of dehydrotetrahedrane (LXXXIV), to a transition state; however, the latter is not that of the isomerisation reaction (LXXXVIIIa) ⇌ (LXXXVIIIb) but of another reaction[239]].



2. Pentalene

Unsubstituted pentalene has not so far been obtained, but many of its substituted derivatives are known (see the relevant reviews[236,237]). In particular, 2-methylpentalene, which is extremely unstable and shows a very great tendency towards dimerisation, has been obtained at −195 °C under the conditions of matrix isolation.[248] Comparison of the electronic spectra of methylpentalene,[248,249] 1,3-dimethylpentalene,[250] as well as the electronic and photoelectron spectra of 1,3,5-tri-t-butylpentalene[251–255] with the results of quantum-chemical calculations[252–255] supports the formation of a structure of type (LXXVIII) with unequal bond lengths. X-Ray diffraction study of 1,3,5-tri-t-butylpentalene led to the same conclusion.[256] The pentalene structure (XCII) with D_{2h} symmetry is subject to lattice instability[129] and has a higher energy than the C_{2h} structure by 25.9 kJ mol^{-1} (NDDO method[252]), by 14.6 kJ mol^{-1} (PPP method[255]), by 46.0 kJ mol^{-1} (CNDO/2 method[86]), but 56.1 kJ mol^{-1} (MINDO/3 method[255]), but 46.4 kJ mol^{-1} (MNDO method[240]), and by 56.9 kJ mol^{-1} (non-empirical calculation, 4-31G//STO-3G basis[254]) and is the transition state in the topomerisation of the latter:



(41)

The experimental barrier to the topomerisation of 1,3,5-tri-t-butylpentalene is 21 kJ mol^{-1} (dynamic NMR [254]). 2,5-Diaza-substitution decreases the barrier to 14.6 kJ mol^{-1} (MINDO/3 method[255]). We may not that the activation energy for the topomerisation of the heptalene structure with C_{2h} symmetry is 108.3 kJ mol^{-1} (MNDO method[240]), which is twice as high as the corresponding value for pentalene.

In the calculations for pentalene by the PPP method, solutions corresponding to structures with C_{2h} and D_{2h} symmetry as well as one with D_{2h} symmetry but with a very long transannular bond (HOMO) having a_u symmetry have been obtained depending on the initial density matrix.[125] The inversion of the frontier π MO is characteristic of solutions corresponding to structures with D_{2h} symmetry. According

to the results of non-empirical calculations in terms of the 4-31G basis (the UHF approximation),[254] the energy of the T_1 state of the pentalene structure with D_{2h} symmetry is lower by 7.1 kJ mol^{-1} than the energy of the electronic singlet state. Here one must bear in mind that an unduly low energy of states with higher multiplicity is usually obtained in terms of the UHF approximation.

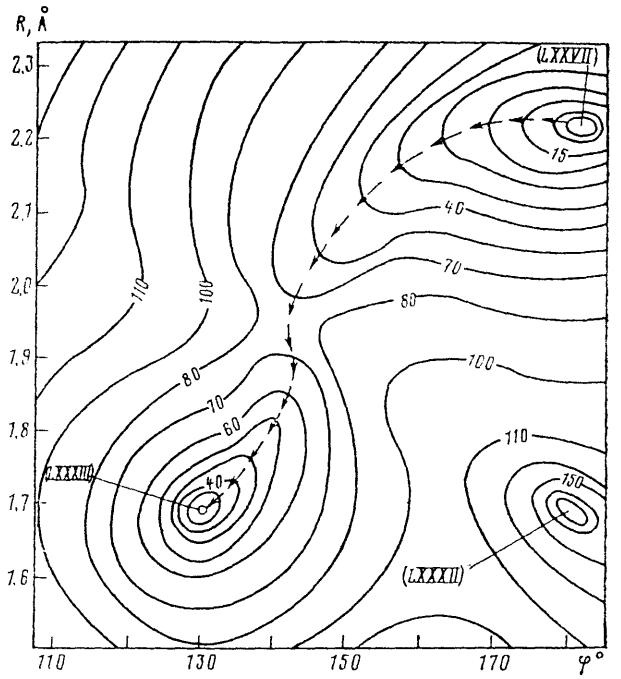
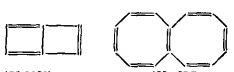


Figure 9. Potential energy surface for the isomerisation reaction of propalene with C_{2h} symmetry [(LXXVII) → (LXXXIII)]; the pathway corresponding to the minimum energy of the reaction is indicated by arrows. The numbers in the gaps in the lines represent the energies (in kJ mol^{-1}) relative to that of the propalene C_{2h} structure; ϕ is the dihedral angle between the C(1)C(2)C(4) and C(1)C(2)C(3) planes [for the significance of the numbering, see reaction (38)]; R is the distance between the C(1) and C(2) atoms.[239]

IV. ALTERNANT [n]ANNULENO-[n]ANNULENES CONTAINING INTERNAL OR PERIMETRIC $4k\pi$-ELECTRON RINGS

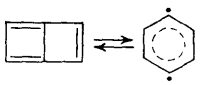
Naphthalene can be regarded as a bridged (transannular bond) analogue of [10]annulene [a$(4n + 2)\pi$-electron system]. We shall consider the cause of the lability of butalene (XCIII) and octalene (XCIV), whose analogues are also $(4n + 2)\pi$-electron systems, namely benzene and [14]-annulene, but they contain internal $4k\pi$-electron rings.



(XCIII) (XCIV)

The study of these cyclic compounds is of interest because it makes it possible to discover the rules governing the influence of the internal rings on the properties of the system as a whole.

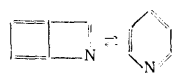
Despite the presence of six π electrons, butalene is nevertheless extremely unstable and its formation only as an intermediate is postulated.[257,258] Calculation of the resonance energy indicates the antiaromaticity of butalene, which contains two cyclobutadiene fragments (Table 1), although its extent is smaller than for cyclobutadiene. Consequently, in this instance the influence of the individual rings prevails over the cyclic conjugation effect along the periphery of the system (six π electrons). At the same time, the contribution of the six-membered $(4n + 2)\pi$-electron butalene ring to the overall exaltation of the diamagnetic susceptibility determines the diatronic character of the antiaromatic system under consideration.[66] Calculations by the MINDO/3 method have shown that the butalene structure corresponds to a minimum on the potential energy surface for the C_6H_4 system.[247] The isomerisation of butalene to p-benzyne (XCV) (isomerism involving bond extension) is allowed by the orbital symmetry conservation rules:[259]



(XCIII) (XCV) (42)

The activation barrier in the given reaction has been estimated as 19.2 kJ mol^{-1}.[247] The difference between the energies of butalene and p-benzyne is 150.2 kJ mol^{-1} according to the results of calculation by the MINDO/3 method. It also follows from the results of non-empirical calculations in terms of the 4-31G basis that butalene corresponds to a minimum on the potential energy surface, but the above energy difference between structures (XCIII) and (XCV) amounted to 323 kJ mol^{-1}.[260]

Monoaza-substitution of butalene does not result in a significant stabilisation of the molecule. The energy difference between 2-azabicyclo[2.2.0]hexa-1,3,5-triene (XCVI) and 2,5-bisdehydropyridine (XCVII) has been estimated as 172 kJ mol^{-1} (by the MNDO method).[261] The activation barrier in the extremely exothermic isomerisation reaction (43) (ΔH = −172 kJ mol^{-1}) is 15.9 kJ mol^{-1}.



(XCVI) (XCVII) (43)

Detailed calculations for octalene (XCIV), which has a nonplanar structure,[262] have not been made.

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The advances achieved in the theory of the chemical structure of antiaromatic systems have promoted further progress in the experimental and theoretical methods for the investigation of molecules. As a result, antiaromatic compounds which had not existed earlier, such as, for example, cyclobutadiene, have become entirely real objects for experimental study.

Bearing in mind the position occupied by the theory of aromaticity–antiaromaticity in the conceptual system of organic chemistry and the multiplicity of ways in which the essential feature of this concept is reflected in various theoretical ideas, it is to be expected that further study of antiaromatic molecules will deepen our understanding of the structure of conjugated organic molecules and will help in the solution of the key problem of the relation between the structures and properties of compounds.

During the preparation of the review for the press, two studies which in our view are of significant interest were published. On the basis of a model calculation of the tunnelling rate constant, Carpenter[263] showed that the contribution of the tunnel mechanism to the automerisation of cyclobutadiene ($D_{2h} \rightleftharpoons D_{4h} \rightleftharpoons D_{2h}$) at temperatures below 0 °C may be more than 97%, determining the low activation entropy, in agreement with experimental data.

Jug[264] proposed a method for the estimation of aromaticity based on the calculation of the total ($\pi + \sigma$) bond order as a weighted sum of the eigenvalues of the two-centre components of the density matrix and demonstrated its relation with π-electron ring currents, which constitute a magnetic criterion. This approach makes it possible, in principle, to consider any compounds, avoiding the limitations of the schemes considered above (DRE, HSRE, TRE). At the same time, the necessity for the preliminary calculation of the optimised molecular geometry undoubtedly significantly complicates the application of this criterion of aromaticity–antiaromaticity.

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New Chemical Agents for Protection against Ionising Radiation

V.G.Yashunskii and V.Yu.Kovtun

Data obtained in the search for radioprotectants among organic monomeric compounds during the period from 1974 to 1983 are surveyed.
The bibliography includes 332 references.

CONTENTS

I. Introduction	76
II. Sulphur-containing compounds-derivatives of β-mercaptoethylamine	76
III. Other sulphur-containing compounds	82
IV. Heterocyclic compounds	83
V. Compounds of diverse structure	88

I. INTRODUCTION

Despite the extremely modest advances achieved as a result of many years of studies undertaken to find new chemical means for protection against ionising radiation, the interest in this problem has not weakened. Interesting monographs[1,2] and reviews,[3-7] devoted to the search for, synthesis, and applications of chemical radioprotectants, have been published in recent years but they cover data obtained over a long period or deal with only individual aspects of this question. Since the need for the search for chemical prophylactic radioprotective agents has increased every year, it is of interest to follow the development and characteristics of the research in this field during recent years.

A review published in 1975[8] summarised the results of the search for chemical radioprotectants during the period between 1968 and 1973. This review surveys and gives a systematic account of the literature data obtained in the search for prophylactic antiradiation agents among new organic monomeric compounds published during the last ten years (from 1974 to 1983 inclusive).

So far as possible, the entire data have been arranged systematically in a manner analogous to that employed in an earlier review.[8]

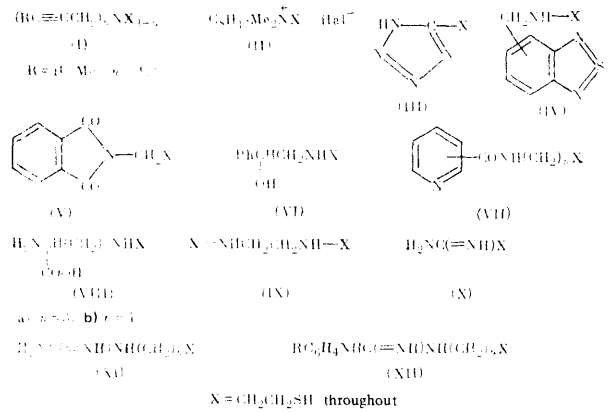
II. SULPHUR-CONTAINING COMPOUNDS—DERIVATIVES OF β-MERCAPTOETHYLAMINE

Recently, new structural analogues and various derivatives of one of the oldest and most widely known radioprotectant—β-mercaptoethylamine (MEA) have appeared. The simple fragment $\rangle N-\overset{|}{C}-\overset{|}{C}-S-$ constitutes the basis of the *N*- and *S*-substituted derivatives synthesised: thiols, disulphides, thiosulphates, phosphorothioates, isothiuronium salts, thiazolidines, etc. The available data will be considered in this sequence.

1. Aminoalkanethiols

The syntheses of a series of MEA derivatives with an unsubstituted thiol group containing various substituents at the nitrogen atom have been described. It has been observed that, among compounds with unsaturated hydrocarbon groups, the alkyl derivatives, for example compound (I), have proved to be the most active and least toxic.[9] It has been shown that the radioprotective effect (RPE) is reduced on quaternisation of the amino-group as in compound (II)[10] and after the introduction of heterocyclic residues—the tetrazolyl [compound (III)[11]], benzo-2,1,3-thiadiazolylmethyl [compound (IV)[12]], phthalimide [compound (V)[13,14]], and 2-hydroxy-2-phenylethyl [compound (VI)[15]] residues.

N-Pyridinoyl derivatives (VII) have been proposed as radioprotectants.[15]



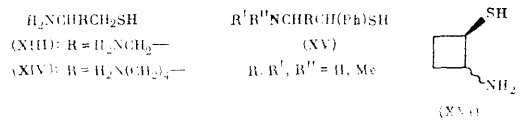
X = CH_2CH_2SH throughout

The MEA derivatives obtained as a result of multistage synthesis, namely the ornithine derivative (VIIIa) and the lysine derivative (VIIIb), have different protecting effects on irradiated mice:[16] compound (VIIIa) administered intraabdominally (i/a) in a dose of 150–300 mg kg^{-1} ensures a 50–100% survival rate, whilst compound (VIIIb) is inactive. Neither compound is effective when administered perorally (p/o).

Compound (IX),[17] which exhibits an antioxidant activity, has been proposed as a radioprotectant.

The replacement of the amino-group in MEA by the amidine group as in compound (X) leads to an appreciable increase of the radioprotective effect and to a decrease of toxicity.[18] In order to investigate antiradiation properties, a series of mercaptoalkylguanidines have been synthesised—unsubstituted [compound (XI)[13]] and aryl-substituted [compound (XII)[19]]. Among them, compounds (XI, $n = 0$) and (XII, R = H, $n = 1$) proved to be the most active.

MEA analogues with various substituents in the hydrocarbon chain have been described. The introduction of the aminomethyl residue at the carbon atom nearest to the nitrogen atom in MEA [compound (XIII)] entails a sharp decrease of activity, while the aminobutyl analogue (XIV) is highly effective in small doses administered intra-abdominally and perorally, although its toxicity is much higher.[20]



It has been shown in experiments on mice[21] that in the series of *C*-phenyl-substituted MEA derivatives (XV), substitution of the hydrogen atoms at the C and N atoms by methyl groups results in a decrease of the radioprotective activity. The introduction of the mercaptomethyl group at one of the carbon atoms in the MEA molecule does not enhance the protecting effect.[22]

The relation between the RPE and structure has been investigated[23] for a series of cyclic MEA analogues—derivatives of *cis*- and *trans*-2-amino-1-mercaptocyclobutane (XVI) and their analogues. The greatest RPE was exhibited by the *cis*-isomers of compound (XVI) when they were administered intra-abdominally or enterally. Analogous cyclopropyl derivatives have also been studied.[24] A series of MEA derivatives having substituents at the sulphur atoms have been synthesised and it has been shown that the introduction of an unsaturated substituent, as in compound (XVII), results in the disappearance of the protecting effect.[9] Compounds having an amidinoethyl substituent, as in compound (XVIII), exhibit a moderate RPE.[25] It is of interest that the introduction of an acetyl substituent into compound (II) to give compound (XIX) decreases the toxicity but the radioprotective properties are preserved.[10]

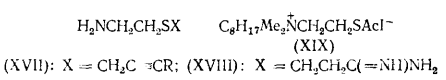


Table 1. Comparative effectiveness of MEA and compound (XIV).[24]

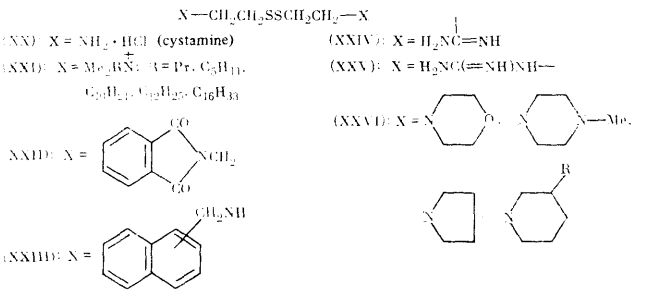
$H_2NCHRCH_2SH$		LD_{50}, mg kg^{-1}	ED, mg kg^{-1}	% protection	*I*
MEA.HCl	i/p	250	150	87	3.1
(R = H)	p/o	615	300	73	3.6
(XIV).2HCl	i/p	88	25	90	6.5
[R = $H_2N(CH_2)_4$]	p/o	450	75	70	10

Notation. LD_{50} is the dose of the test substance which results in the death of 50% of animals and ED is the effective dose. *I* = protectant index.

The number of closest MEA analogues (mercaptoalkylamines) investigated in recent years is small—approximately 50 (during the previous period 1968–1970, about 130 of these were described); among these compounds, one merits attention, namely 2,6-diaminohexane-1-thiol (XIV). Its advantage over MEA is clearly seen from the data in Table 1.

2. Aminoalkyl Disulphides

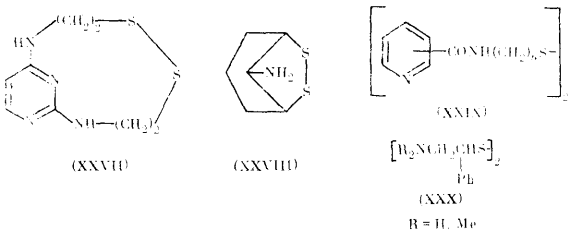
The interest in the search for more effective cystamine (XX) analogues has not weakened. It has been confirmed[10] that the replacement of the free amino-groups in the molecule of compound (XX) by quaternary ammonium groups, including those incorporating higher alkyl groups, as in compound (XXI), results in a decrease of the RPE. The same result has been obtained[13] when the amino-groups were substituted by phthalimidomethyl residues (XXII). The 1- and 2-naphthylmethyl derivatives of cystamine (XXIII) proved to be inactive:[12]



The bisamidine analogue (XXIV)[18] and the bisguanidine analogue (XXV)[13] of cystamine are not inferior to the latter as regards activity.

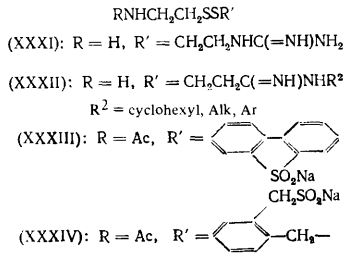
A pronounced radioprotective activity has not been observed in a whole series of bis(aminoethyl) disulphides containing at the nitrogen atoms heterocyclic substituents such as the 2-quinoxalinyl,[27] benzo-2,1,3-thiadiazol-4-ylmethyl and the corresponding 5-methyl,[12] 2-pyridylmethyl,[27] 2-pyrimidinyl,[27,28] and phenyltetrazolyl[27] groups. On the other hand, it has been observed that compounds of the type of (XXVI) with the morpholine and 4-methylpiperazine groups exhibit an RPE which is not inferior to that of unsubstituted cystamine.[27,28]

The macrobicyclic disulphide (XXVII),[29] the bicyclic disulphide (XXVIII),[30] and the disulphides containing pyridinecarboxylic acid residues (XXIX)[15] have been described as radioprotective agents.



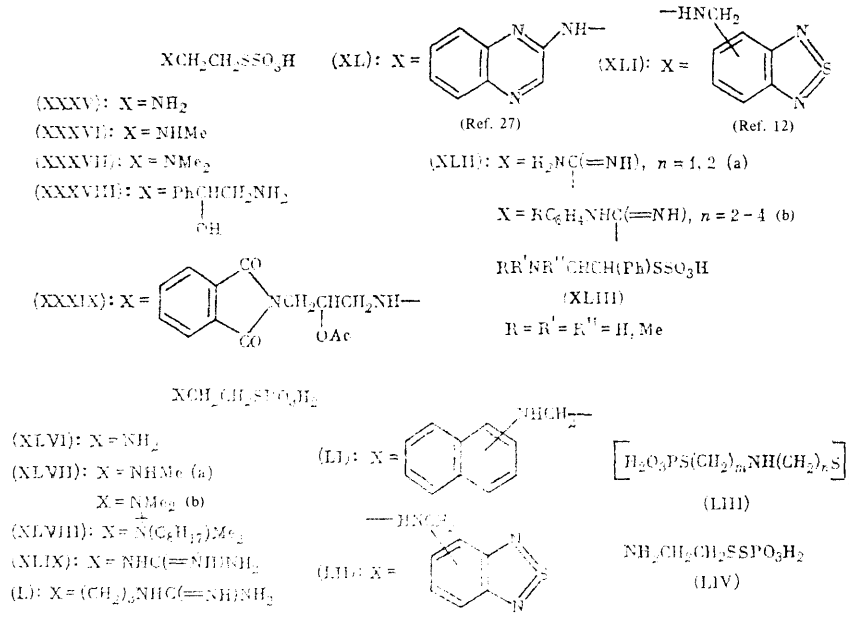
A fairly distinct antiradiation effect has been exhibited by certain *C*-phenyl-substituted cystamines (XXX).[21,31]

Interesting results have been obtained in a study of the asymmetric disulphides (XXXI),[13] (XXXII),[32,33] (XXXIII), and (XXIV),[34] containing the aminoethyl fragment. Thus the last compound is superior in its activity to the disulphide (XX) and all the analogues quoted above; its LD_{50} (for i/a and p/o administration) is greater than 900 mg kg^{-1} and ensures 100% protection of mice against the absolutely lethal radiation dose when administered intra-peritoneally in a dose of 75 mg kg^{-1}; when taken orally the dose is 600 mg kg^{-1}



3. Aminoalkyl Thiosulphates

Much less attention than in previous years has been devoted to derivatives of *S*-aminoethylthiosulphuric acid (XXXV) (Bunte salts). It has been found that methylation of the nitrogen atom, as in compounds (XXXVI) and (XXXVII), results in an appreciable enhancement of the protecting activity:[35,36]



As for other MEA derivatives, the introduction of the naphthylmethyl residue at the nitrogen atom eliminates the protecting effect almost completely.[12] Compounds (XXXVIII) and (XXXIX) also showed a low activity.[14] Like the disulphides, the majority of Bunte salts with heterocyclic substituents at the nitrogen atom proved to be inactive and only compounds (XL) and (XLI) led to 60–70% survival rate of mice and only after administration in near-toxic doses.

The amidine [compound (XLIIa)[18]] and arylguanidine [compounds (XLIIb)[19]] derivatives have been investigated. Compound (XLIIa, $n = 2$) is somewhat superior to compound (XXXV) as regards activity.

C-Phenyl derivatives (XLIII) showed a pronounced protecting effect.[21,31]

It is noteworthy that a much greater number of compounds with a similar structure were investigated in the previous period and among them highly effective radioprotectors were discovered.[8]

4. Aminoalkyl Phosphorothioates

The main trend in studies in this field involves the discovery of radioprotectants most promising for practical use in cancer X-radiotherapy and not the synthesis of new compounds.[37–39] Among a series of other compounds, *S*-[*N*-(3-aminopropyl)-2-aminoethyl]phosphorothioic acid (gammaphos, WR-2721), which is at present undergoing clinical tests in the USA and Japan, has attracted special attention.[40,41]

Several studies have been devoted to the synthesis and investigation of the RPE of derivatives of polyaminopolyalkyl phosphorothioates widely represented in the previous period. It has been shown that the introduction of the hydroxy-group into the hydrocarbon chain (see Table 2) does not as a rule reduce the RPE after intra-peritoneal administration to mice, but these substances do not protect when administered orally.[14,37,39]

Table 2. The radioprotective activity of $RSPO_3H_2$ administered intra-peritoneally to mice.[14]

R	LD_{50}, mg kg^{-1}	ED, mg kg^{-1}	% protection
$H_2N(CH_2)_3NHCH_2CH(OH)CH_2$—	875	200	100
$H_2NCH_2CH(OH)CH_2NH(CH_2)_2$—	825	300	93
$H_2NCH_2CH(OCOMe)CH_2N(CH_2)_2$—	>1250	500	100
$H_2NCH_2CH(OH)CH_2NH(CH_2)_3$—	>700	600	100
$HO(CH_2)_2NH(CH_2)_2NH(CH_2)_2$—	200	100	60
$H_2NC(CH_2OH)_2CH_2$—	>1250	250	100
$H_2N(CH_2)_2NH(CH_2)_2$— (XLIV)	1020	300	100

The introduction of an additional aminoalkyl group increases the toxicity and decreases somewhat the RPE of compounds (XLV) compared with compounds (XLIV); the greatest dose reduction factor (DRF), amounting to 1.8, is

shown by compounds with $l = m = n = 2$ and $l = n = 2$, $m = 3$.[42]

$H_2NCH_2CH_2CH_2NHCH_2CH_2SPO_3H_2$
(XLIV)
$H_2N(CH_2)_l NH\,(CH_2)_m\,NH(CH_2)_nSPO_3H_2$
(XLV)

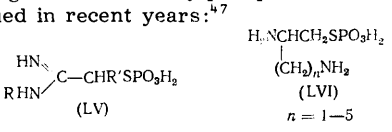
It has been found that the replacement of the hydrogen atoms by the methyl group, as in compound (XLVIIa), at the nitrogen atom of aminoethylphosphorothioic acid (XLVI) does not decrease the RPE; the presence of two methyl groups results in the loss of radioprotective properties by compound (XLVIIb),[35] but the introduction of an additional octyl substituent, as in compound (XLVIII), enhances the RPE with a slight increase of toxicity.[10]

It has been reported[43] that the guanidine derivatives (XLIX) and (L) exhibit a radioprotective activity. As for the aminoalkanethiols and disulphides, the naphthylmethyl derivatives (XLI) proved to be inactive.[12] *N*-Benzo-2,1,3-thiadiazolylmethylaminoethylphosphorothioic acids (XLII) showed the highest RPE.[12]

It was found[44] that the nature of the cation linked to compound (XLVI) has different effects on the toxicity and radioprotective activity; the piperidine and morpholine salts proved to be comparable to sodium salts in terms of their specific activity, while adamantylammonium salts proved to be inactive.

It has been shown recently[45] that derivatives of aminoethylphosphorothioic acid, containing the alkyl disulphide group at the nitrogen atom, as in compound (LIII), exhibit radioprotective activity in doses of 12.5–200 mg kg^{-1}. A new type of phosphorothioic acid derivatives has been discovered and investigated by Sverdlov and co-workers,[46] who showed that the disulphide (LIV) protects up to 55% of mice against radiation over a period of 15–60 min when introduced intra-peritoneally. An approximately the same effect has been obtained also in the case of gamma-neutron irradiation. The substance is inactive when introduced enterally.

Studies designed to search for radioprotectants among amidine analogues of aminoethylphosphorothioic acid (LV) have continued in recent years:[47]


(LV)

(LVI)
$n = 1$—5

R = H, R′ = Alk
R′ = H, R = 1-adamantyl (Ad),
3-Me=Ad, 3, 5, 7-Me_3=Ad

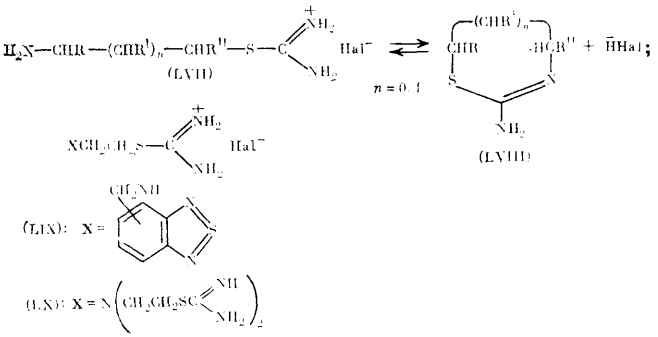
It has been shown that the replacement of the hydrogen atom at the carbon atom by the methyl group, as in compound (LV, R′ = Me), hardly affects the toxicity of the protecting effect when introduced intra-peritoneally but in the enteral administration the toxicity is reduced by a factor of ~1.5, while the effective protective dose increases by approximately the same factor. With increase of the bulk of the group R′, the toxicity of the compounds increased with a simultaneous reduction and even loss of radioprotective activity. Unexpectedly, it was found that the introduction of methyl groups into the adamantyl group results in only a sharp increase of toxicity in the complete absence of a protecting effect (possibly owing to the sharp reduction of solubility in water).

The antiradiation activity of *C*-aminoalkyl derivatives (LVI) has been investigated[20] and it has been shown that they are not inferior in this respect to compound (XLVI) when introduced intra-peritoneally, but, with the exception of compound (LVI, $n = 4$), they are all inactive when introduced enterally. It is of interest that the *L*-isomers of compounds (LVI, $n = 3$ or 4) showed no differences as regards the RPE compared with the corresponding racemates. Table 3 presents data for compounds of this series.

5. Aminoalkylisothiuronium Salts

A number of studies have been devoted to the synthesis and radioprotective properties of derivatives of 2-aminoethylisothiuronium (AET) (LVII, R = R′ = R″ = H, $n = 0$), including cyclic compounds.

The toxicity and radioprotective activity of various *N*- and *C*-substituted AET (LVII, $n = 0$ or 1) and the corresponding cyclic forms, namely 2-aminothiazolines and 2-aminothiazines (LVIII, $n = 0$ or 1), have been investigated.[48–51] It has been shown that the cyclic forms, which are the products of the metabolism of AET derivatives in the organism, are less active as radioprotectants; all new compounds are inferior to AET in their antiradiation activity but they exhibit a broader spectrum of therapeutic activity and the duration of their RPE is longer.


(LVII)

(LVIII)

(LIX)

(LX)

Table 3. The radioprotective activity of compound (LVI) in mice.[20]

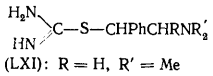
n	Method of administration	LD_{50}, mg kg^{-1}	ED, mg kg^{-1}	% protection	*I*
1	i/p	>900	400	80	>4
2	i/p	>1250	250	100	>10
3	i/p	>1000	250	100	>8
4	i/p	325	62.5	80	9.4
	p/o	750	500	80	2.7
5	i/p	500	200	100	5
	p/o	>1000	400	30	>3
(XLIV)	i/p	1020	300	100	6.8
	p/o	1500	600	100	5

It has been found in relation to *S*-(2-aminopentyl)isothiuronium salts (LVII, R = Pr, R′ = R″ = H, $n = 0$) that[52] both the optical isomers of this compound and the racemic form exhibit a pronounced RPE in experiments on cells but hardly protect irradiated mice. The *N*-benzo-2,1,3-thiadiazolinyl-3-methyl derivative of AET (LIX)[12] as well as the unusual tri-isothiuronium derivative (LX)[53] showed a weak RPE.

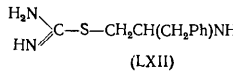
It has been shown[54–56] that the adenosine triphosphate salt of AET (adeturon) exhibits a high radioprotective activity under the conditons of acute irradiation and also in prolonged and fractionated irradiation. In experiments on monkeys 50% protection was achieved after intravenous

administration in a dose of 150 mg kg^{-1} 6–15 min before irradiation.

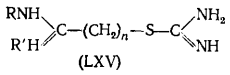
Interesting results have been obtained by modifying the carbon chain of AET with aryl substituents. Compounds (LXI)[21,31] and (LXII)[31] exhibit a high RPE, but the replacement of a hydrogen atom in compound (LXI) by the methyl group, as in compound (LXIII), or the replacement of the dimethylamino-group by the piperidino-group, as in compound (LXIV), fully abolishes the radioprotective properties of the molecule.[21]



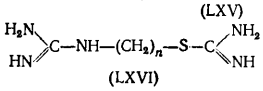
(LXI): R = H, R′ = Me
(LXIII): R = R′ = Me
(LXIV): R = H, R′ = $(CH_2)_5$



(LXII)



(LXV)



(LXVI)

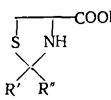
A series of AET derivatives in which the amino-group has been replaced by the amidino-group, as in compound (LXV),[18,57,58] or the guanidino-group, as in compound (LXVI),[19] have been synthesised. The synthesis and the radioprotective activity of compounds in the (LXV) series with different substituents at the nitrogen atom of the amidino-group and also with different lengths of the carbon chain have been studied in detail[57,58] and it has been shown that, when R = R′ = H, compounds with n = 1 or 3 are effective, while those with an even number of methylene groups are completely inactive. Among derivatives (LXV) substituted at both nitrogen atoms, the compound with the 2-methoxyphenyl residues showed the highest activity.[58]

Compounds in which the isothiuronium group is included in a ring will be considered together with other heterocyclic compounds.

6. Thiazolidines

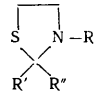
In contrast to other derivatives of mercaptoethylamine, more studies have been devoted to its cyclic analogues, namely thiazolidines, than in the previous period. These compounds have attracted attention because some of them are capable of protecting animals when administered several hours before irradiation,[4,59] showing at the same time a broad spectrum of therapeutic activity.[60]

It has been shown[59,61,62] that, among derivatives of 2,2-dialkylthiazolidine-4-carboxylic acid (LXVII), the methyl esters (LXVII, a and b) are greatly inferior to the corresponding ethyl esters (LXVII, c and d) as regards the RPE. The ester (LXVIId) proved to be an effective radioprotectant; its hydrochloride (LD_{50} = 1750 mg kg^{-1}) ensured 90% protection of mice when administered intra-peritoneally in a dose of 813 mg kg^{-1} 15–30 min before irradiation:[59,61]



(LXVII)

a) R = R″ = Me, R′ = Et; b) R = R′ = R″ = Me; c) R = R′ = Et, R″ = Me; d) R = Et, R′ = R″ = Me; e) R = R″ = Me, R′ = CH_2COOEt; f) R = Et, R′ = COOEt, R″ = Me; g) R = H, R′R″ = $(CH_2)_n$ (n = 5–7); h) R = Et, R′ = H, R″ = CHPhCOOEt



(LXVIII)

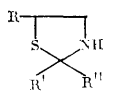
R = H, COOEt; R′ = Me, Pr, Ph
R″ = CH_2COOEt, $CH(CH_2Ph)COOEt$

The introduction of the ethylcarbonylmethyl [compound (LXVIIe)], ethoxycarbonyl [compound (LXVIIf)], or ethoxycarbonylphenylmethyl [compound (LXVIIh)] residues in the 2-position in place of the alkyl group full abolishes activity.[53,61] The absence of protection has been observed[63] also for the products of the condensation of cysteine with cyclic ketones (LXVIIg).

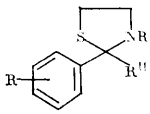
Comparison of the toxicities and radioprotective activities of the alkyl esters of 2,2-dimethylthiazolidine-4-carboxylic acid (LXVIII, R = alkyl, R′ = R″ = Me) and the corresponding cysteine esters showed[62] that the latter are less toxic and their radioprotective activity is higher. The esters of lower alcohols (ethyl and propyl) proved to be less toxic in both series.

A series of compounds containing the ethoxycarbonylmethyl group in the 2-position in the thiazolidine ring [compounds (LXVIII)] have been synthesised and investigated.[64] Among them, compound (LXVIII, R = H, R′ = Pr, R″ = CH_2COOEt) proved to be the most active. After the introduction of the ethoxycarbonyl group at the nitrogen atom, which increases the stability of the heterocycle, a fairly pronounced effect is maintained in the methyl derivative (LXVIII, R = COOEt, R′ = Me, R″ = CH_2COOEt).

Interesting results have been obtained in the study of thiazolidines without carboxy-groups. The high effectiveness of 2,2,5-trimethylthiazolidine (LXIX), whose hydrochloride protects 90% of mice irradiated with an absolutely lethal dose after intra-peritoneal administration in a dose of 500 mg kg^{-1} (LD_{50} = 1150 mg kg^{-1}) during periods from 2 to 60 min before irradiation.[59]



(LXIX): R = R′ = R″ = Me;
(LXX): R = H, R′ = Me, R″ = Et;
(LXXI): R = H, R′ = H, Me, R″ = Alk, alkenyl, alkynyl



(LXXII)
R = H, Hal, OH, Me, MeO;
R′, R″ = H, Me

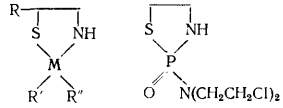
(LXXIII)
R = H, Alk, Ar

Its isomer (LXX) has a somewhat lower activity and is more toxic (LD_{50} = 845 mg kg^{-1} for the hydrochloride).[59] It has been found that the RPE increases with increase of the degree of unsaturation of the substituent R″, as in compound (LXXI).[9]

Among 2-arylthiazolidines (LXXII) (more than 30 compounds), substances have been found, namely compounds [LXXII, R′ = R″ = H, R = 3-F, 3,4-$(OMe)_2$ or R = 4-OMe, R′ = Me, R″ = H], which exhibit a pronounced antiradiation activity,[60,65,66] The authors were unable to establish a relation between the rate of hydrolysis of these compounds, leading to the liberation of free MEA, and the radioprotective activity.[65,67] 2-(4- and 5-Benzo-2,1,3-thiadiazolinyl) derivatives exhibited a low level of protection.[12] A series of monosaccharide derivatives of thiazolidine have been described.[68]

Six-membered homologues of thiazolidines, namely perhydro-1,3-thiazines (LXXIII), containing alkyl and aryl substituents in the 2-position,[69] are of undoubted interest: among the 16 compounds of this series which have been synthesised, several highly effective radioprotectants (LXXIII, R = H, Ph, 4-FC_6H_4, 3-BrC_6H_4, or 2-MeC_6H_4) have been discovered. It has been observed that the RPE of the bases and the hydrochlorides are very different; thus, for R = Me, Pr, or 2-MeC_6H_4, the free bases show a much higher activity than the hydrochlorides, but, when R = 4-FC_6H_4 or 3-BrC_6H_4, the hydrochlorides are more effective.[69]

The RPE of several thiazolidines in which the carbon atom in the 2-position has been substituted by heteroatoms have been studied. In experiments on cell cultures[67] and on mice[70] it has been shown that germanium derivatives (LXXIV)[67,70] have higher RPE than all the thiazolidine derivatives investigated previously but are more toxic. Silathiazolidines exhibit a high RPE.[70]



(LXXIV)
R = H, Me; R′ = R″ = Alk
M = Ge, Si

(LXXV)

It has been shown that the anticancer preparation cyclophosphamide (LXXV) is inactive when introduced intraperitoneally 1–24 h before irradiation, but, when it is administered 2–4 days ahead, it protects 50% of the lethally irradiated animals.[71]

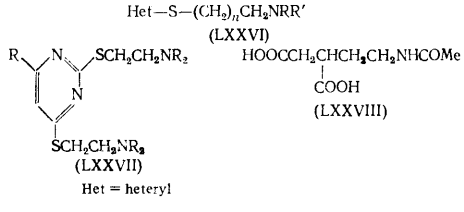
An unusual outcome of the search for radioprotectants in the thiazolidine series carried out in the previous period has been the establishment of correlations between the radioprotective activity and the calculated electron density at the sulphur and nitrogen atoms[72] and also structural factors (calculation by the Free–Wilson method).[73]

Thus, several substances with a high radioprotective activity have been found among fairly large numbers of thiazolidine derivatives synthesised and investigated.

7. Other Derivatives of Mercaptoalkylamines

This Section deals with compounds synthesised and investigated as potential radioprotectants whose structure is more remote from that of MEA and which were not included in the previous Sections. These are derivatives of mercaptoalkylamines with non-functional substituents at the sulphur atom and also with a modified hydrocarbon chain, including those where the chain is incorporated in a cyclic system or contains a carbonyl group.

Among the large group of *S*-heteryl-substituted mercaptoalkylamines (LXXVI),[74–79] the highest activity (up to 70–90% survival rate) was shown by compounds with hydroxypyrimidine[74] and quinazoline[74,78] rings as well as di-substituted pyrimidines (LXXVII).[74] The succinic acid derivatives (LXXVIII)[80] have a similar activity.

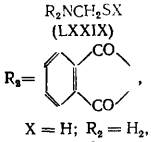


Het—S—$(CH_2)_nCH_2NRR'$
(LXXVI)

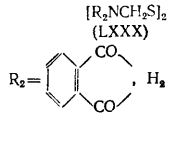
(LXXVII)
Het = heteryl

(LXXVIII)

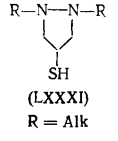
Derivatives of mercaptomethylamine (LXXIX) and (LXXX)[81] are of interest, but the results of biological studies are not presented in the relevant communication.



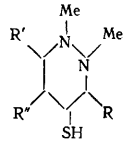
R_2NCH_2SX
(LXXIX)
X = H; R_2 = H_2,
X = SO_3H



$[R_2NCH_2S]_2$
(LXXX)



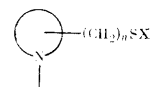
(LXXXI)
R = Alk



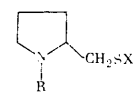
(LXXXII)

Another unusual group of mercaptoalkylamine derivatives are compounds in which the nitrogen atom is incorporated in a heterocyclic ring. Among compounds of the type of (LXXXI) and (LXXXII),[82,83] none have been found with radioprotective activity.

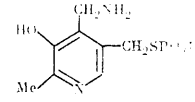
At the same time highly effective radioprotectants have been discovered among nitrogen-containing heterocycles in which the *S*-functional group is in the side chain, as in compound (LXXXIII):



(LXXXIII)



(LXXXIV)
X = SO_3H, PO_3H_2, C(=NH)NH_2
a) R = H, X = PO_3H_2;
b) R = Me, X = PO_3H_2



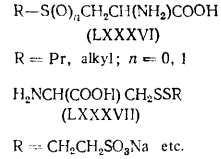
(LXXXV)

The heterocyclic system in these compounds is represented by the pyrrolidine [compound (LXXXIII)[35,36]], imidazole,[84] tetrazole,[11] pyridine,[85,86] pyrimidine,[87,88] and benzimidazole[87] rings.

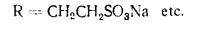
Perhaps the most interesting result has been obtained in the study of the phosphorothioic derivatives (LXXXIV). It was shown[35] that compound (LXXXIVa) has a high RPE, while the replacement of the hydrogen atom by the methyl group, as in compound (LXXXIVb), entails the loss of activity.

Comparison of the rates of hydrolysis of the phosphorothioate to the thiol and of the RPE for different time intervals between the administration of compound (LXXXIVa) and irradiation of mice led to the conclusion that there is no relation between these quantities. Pyridoxamine phosphorothioate (LXXXV) also gives rise to a high RPE.[86]

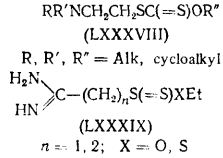
Derivatives of cysteine, namely esters,[62] sulphides and sulphoxides (LXXXVI),[89] and di- and poly-sulphides (LXXXVII)[90] have been synthesised as potential radioprotectors.



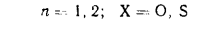
R—$S(O)_nCH_2CH(NH_2)COOH$
(LXXXVI)
R = Pr, alkyl; n = 0, 1



$H_2NCH(COOH)CH_2SSR$
(LXXXVII)
R = $CH_2CH_2SO_3Na$ etc.



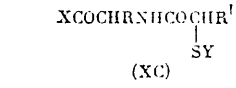
$RR'NCH_2CH_2SC(=S)OR''$
(LXXXVIII)
R, R′, R″ = Alk, cycloalkyl



(LXXXIX)
n = 1, 2; X = O, S

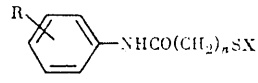
Among xanthates of the type of (LXXXVIII),[91] substances have been discovered which are superior to AET in terms of their RPE; it has been noted that some of them increase the survival rate of mice under the conditions of gamma-neutron irradiation; the amidino-derivatives (LXXXIX) are less active.

The summarising communication by Japanese investigators[92] quotes data concerning a large number of mercaptoalkanoylaminoacids (XC) investigated, which are analogues of mercaptopropionylglycine (XCa) (thiol, meprin, MPG) studied previously. Among them, only the amide (XCb) showed a pronounced radioprotective activity close to that of compound (XCa). Derivatives of MPG, namely compounds (XC, c and d),[93,94] the disulphide (XCe),[95,96] the thiosulphate (XCf),[97] and the phosphorothioate (XCg)[97,98] have been described as radioprotectants.



(XC)

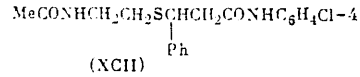
a) X = OH, Y = R = H, R' = Me;
b) X = H_2N, Y = R = H, R' = Me;
c) X = OH, Y = R = H, R' = Alk, Ar, aryl alkyl;
d) X = OH, Y = H, R = Alk, $PhCH_2$, R' = Me;
e) X = OH, Y = SCH(Me)CONHCH$_2$COOH, R = H, R' = Me;
f) X = OH, Y = SO_3Na, R = H, R' = Me;
g) X = OH, Y = PO_3HNa, R = H, R' = Me



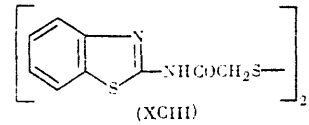
(XCI)

n = 1, 2; X = SO_3Na, C(=NH)NH_2

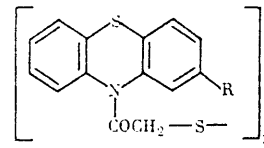
More remote analogues of MPG, among which mention should be made of the *N*-aryl derivatives (XCI)[88] and (XCII)[80,87,99] as well as the disulphides (XCIII)[100] and (XCIV)[101] and the hydrazide (XCV),[22] have also been investigated.



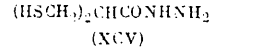
(XCII)



(XCIII)



(XCIV)



(XCV)

Ar—$(CH_2)_n$SX
(C)
X = C(=NH)NH_2·HY, SO_3H; n = 1—3

PhC=CHMe
S—C(=NH)NH_2·HY
(Cl)

RSSC(=NH)NH_2·$^1/_2H_2SO_4$
(CII)
R = $CH_2CH_2SO_3Na$, $CH_2CH(OH)CH_2SO_3Na$

X—$(CH_2)_nCH_2CH_2NRCSSY$
(CIII)
a) R = H, Me; X = NHR, $NHCH_2CH_2NH_2$; Y = H; n = 0, 1;
b) R = H; X = SEt, SO_2Et; Y = Et; n = 0;

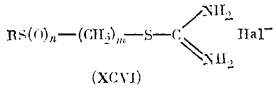
HSSCNR$(CH_2)_n$NRCSSH
(CIV)
R = H, Me; n = 2—4;
$(Alk)_2NCSSNa$
(CV)

III. OTHER SULPHUR-CONTAINING COMPOUNDS

Apart from the compounds in which the aminoalkanethiol structure is repeated, sulphur-containing substances of different structure with or without nitrogen atoms in their composition have been synthesised and investigated in recent years as potential antiradiation agents.

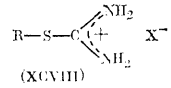
The synthesis of radioprotectants having the isothiuronium structure is traditional. Thus Japanese investigators achieved the synthesis of a series of isothiuronium derivatives (XCVI),[102] one of which has been obtained independently by Soviet workers.[103] A series of di-isothiuronium compounds (XCVII) have also been obtained independently by Japanese and Soviet investigators.[53,104,105] A satisfactory correlation between their physical properties and the RPE has been established.[104]

A study has been made of 34 compounds having the isothiuronium structure and containing an organophosphorus anion [compounds (XCVIII) and (XCIX)].[106-111] *S*-Ethylisothiuronium diethyl phosphate and metaphosphate as well as *S*-isopropylisothiuronium metaphosphate showed the highest RPE.[110]



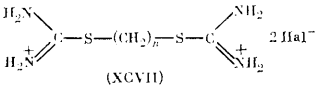
(XCVI)

R = H, Alk; m = 1, 2; n = 0, 2



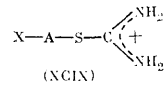
(XCVIII)

R = Alk;
X⁻ = anion of phosphorus-containing acid



(XCVII)

n = 2, 6



(XCIX)

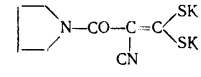
A = alkylene or hydroxy-alkylene;
X = residue of phosphorus-containing acid

Arylisothiuronium derivatives (C) and (CI),[53,87,105] thiosulphuric acid derivatives (C),[87,99] and the disulphides (CII)[90] have been proposed as potential radioprotectants.

Substances with a distinct antiradiation activity have been discovered among derivatives of dithiocarboxylic acids (CIIIa), (CIV),[112,113] (CIIIb),[103] and (CV).[53,105]

Derivatives of 2-*N*-alkoxyiminoalkanethiols (CVI)[114] have been studied as radioprotectants, but they proved to be almost inactive.

RC(=NOR")CHR'SX
(CVI)
R, R' = H, Alk, Ar;
R, R' = alkylene,
R" = Me, Et;
X = COSEt, CSSEt, SO_3Na



(CVII)

1-(3,3-Dimercapto-2-cyanoacryloyl)pyrrolidine (CVII)[27] afforded 80% protection to irradiated mice when administered enterally in a near-toxic dose, but its activity is low when it is administered orally.

Compounds (CVIII) containing the amidine fragment[115-117] exhibit a weak radioprotective activity.

As already stated, the search for prophylactic antiradiation agents has also been conducted among sulphur compounds not containing nitrogen, for example, among the alkyl derivatives (CIX), (CX),[103] and (CXI)[118] as well as aromatic and heterocyclic derivatives (CXII)[81,99] and (CXIII).[119]

PhNHC(=NH)SC(=NH)NHNHCOCH$_3$
(CVIII)

$EtSO_2CH_2CH_2SX$
(CIX)
X = H, PO_3H_2, $SCH_2CH_2SO_2Et$

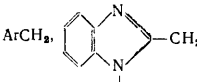
R—$(CH_2)_n$—SX
(CX)
R = Ac, OEt; X = H, PO_3H_2, n = 1, 2

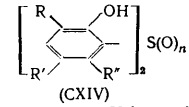
$(RS)_2CHCH_2CH_2SR$
(CXI)

Ar$(CO)_n$—$(CH_2)_m$$SSO_3Na$
(CXII)
n = 0, 1; m = 1, 3

$(RS)_2C=S$
(CXIII)

R = $ArCH_2$,





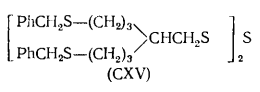
(CXIV)

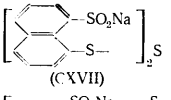
R, R', R" = H, NO_2, Hal; n = 0—2

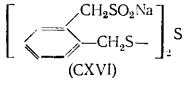
The sulphur-containing bisphenols (CXIV) exhibit a pronounced radioprotective activity[120] (when administered intra-abdominally 1 and 5 h before irradiation), but these data require additional checks, since the substances were introduced in the form of a solution in dimethyl sulphoxide, which is itself known to have a protecting activity.

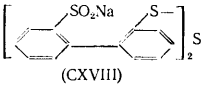
2,3-Dimercaptopropanesulphonic and dimercaptosuccinic acids or their potassium and sodium salts have been proposed as radioprotectants.[121]

5-Thio-D-glucose has been subjected in recent years to extensive studies as a radioprotectant for normal and tumour tissues.[39,122-124]


(CXV)


(CXVII)


(CXVI)


(CXVIII)

The continuation of studies initiated previously on the synthesis and radioprotective activity of a series of trisulphides yielded compounds (CXV)–(CXVII) having an aromatic structure;[34,125] compound (CXVIII) with LD_{50} of 430 mg kg^{-1} when administered intra-peritoneally almost fully protects mice in a dose starting from 4.6 mg kg^{-1}, while all the animals in the control group died.

This substance is less effective when administered orally. The introduction of chlorine atoms into the *meta*-positions relative to the sulphur atoms lowers the activity significantly. The phenyl and particularly the naphthyl analogues (CXVI) and (CXVII) are greatly inferior to the biphenyl compound (CXVIII) as regards activity.

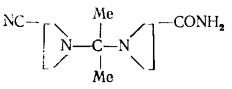
The attempt to find effective radioprotectants among selenium compounds were unsuccessful.[126-130]

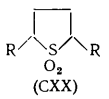
Thus, among sulphur compounds which do not belong to the series of mercaptoethyl derivatives, trisulphides containing residues of sulphinic acid, phosphorus-containing isothiuronium derivatives, and 5-thio-D-glucose are of greatest interest as potential radioprotectants.

IV. HETEROCYCLIC COMPOUNDS

Compared with previous years, there has been a marked growth of interest recently in heterocycles as potential radioprotectants. The main trends in the search for radioprotectants in this extensive branch of organic chemistry have been described in a review.[3]

2-(2-Cyanoaziridino)-2-(2-carbamoylaziridino)propane (CXIX), which ensures a 50% survival rate of mice when administered intra-peritoneally in a dose of 50 mg kg^{-1} two days before irradiation has been proposed for the prophylaxis and treatment of radiation damage.[131-133]

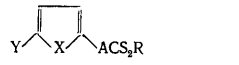

(CXIX)


(CXX)

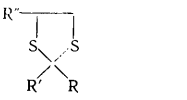
a) R=H; b) R=CH(OH)$CH_2CH_2CONR'_2$, R'=H, Me

It has been observed[134] that sulpholan (CXXa) and its bisbutyramide derivatives (CXXb) exhibit a pronounced radioprotective activity; they are actually superior to MEA (DCF = 1.6). A relation between the electron-donating properties of substances in this series and their radioprotective activity has been found with the aid of quantum-mechanical calculations.

A series of dithiocarbamate derivatives of furan and thiophen [compounds (CXXI)] have been investigated. Among them, only compound (CXXIa) showed a weak RPE, while the remaining compounds are inactive[135]


(CXXI)

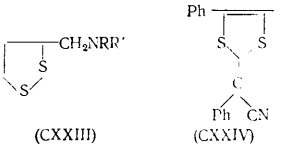
A=SO_2NH, R=Me, X=S, Y=H (a)
A=$C(CN)_2$, SONH; R=Alk, K; X=O, S; Y=H, Cl

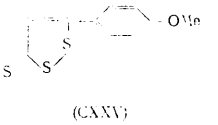

(CXXII)

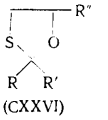
R=Alk, Ph, H; R'=Alk, Ar, Ac; R, R'=alkylene; R''=H, Alk

Continuation of earlier studies on the synthesis and the RPE of dithiolans by French investigators alone yielded 92 new derivatives of this class of heterocycles [compounds (CXXII)],[65] among which 32 afforded more than 50% protection to irradiated mice. It was impossible to establish general structure–activity relations, but certain partial conclusions can apparently be made. Thus the introduction of polar substituents into the 4-position (R'') and of aryl substituents into the 2-position (R) weakens the protecting activity; the presence of cycloalkyl substituents in the 2-position (R') promotes a decrease of activity.[136,137] Among 1,2-dithiolans (CXXIII),[138] effective radioprotectants have not been discovered.

Whereas 1,3-dithiolen (CXXIV)[27] does not exhibit radioprotective activity, there are data for the 1,2-dithio-derivative (CXXV)[139,140] showing that it has been used to protect the central nervous system of human beings against radiation in X-ray therapy.


(CXXIII) (CXXIV)


(CXXV)


(CXXVI)

R=H, Me, SH; R'=H, Me; R, R'=alkylene; R'=H, CH_2Cl

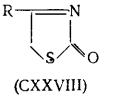
(CXXVII)

R=H, R'=Alk, Ar; R, R''=alkylene; R''=H, Me

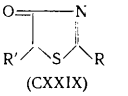
Among 19 1,3-oxathiolan derivatives (CXXVI),[66] 5-chloromethyl-1,3-oxathiolan-2-thiol showed the highest activity; the introduction of an aryl substituent in the 2-position results in a loss of protecting activity. In contrast to this, 1,3-oxazolidines (CXXVII)[65,141,142] exhibit an RPE only in the presence of an aryl substituent in the 2-position; the *m*-chlorophenyl derivative showed the highest activity.

Thiazolidine and 2-aminothiozoline derivatives were examined above.

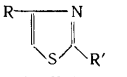
Among 4-hydrazinothiazolin-2-one derivatives (CXXVIII),[143] 5-alkyl-2-aminothiazolin-4-ones[144] and 5-alkyl-2-hydrazinothiazolin-4-ones (CXXIX),[143] compounds affording 30–60% protection to irradiated mice, were found.


(CXXVIII)

R=$NHNH_2$, $NMeNH_2$


(CXXIX)

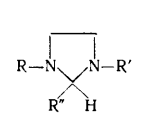
R=NH_2, $NHNH_2$, PhNHN=CH; R'=H, Me, Et, CH_2COOH


(CXXX)

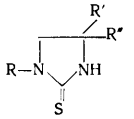
a) R=2,4-$(HO)_2C_6H_3$, Ph; R'=NH_2,
b) R=*m*-ClC_6H_4, R'=NH_2

A fairly high RPE has been discovered for 2-amino-4-arylthiazoles, in particular the phenyl and 2,4-dihydroxyphenyl derivatives (CXXX);[145-147] the replacement of the amino-group by the hydrazino-group entails the loss of activity,[145] while incorporation of the hydrazino-group in the pyrazole ring sometimes almost fully restores the initial level of protection.[148,149] Comparison of the antioxidant properties of the dihydroxyphenyl derivatives (CXXXa) in relation to a model fat and the RPE enabled the authors to conclude that there is no relation between the ability of these compounds to inhibit free-radical processes and their radioprotective activity.[146]

Among 36 imidazolidines, the highest RPE has been found for the 2-(*p*-tolyl) derivative monomethylated at the nitrogen atom [compound (CXXXI)]; alkylation of the second nitrogen atom has an ambiguous effect.[66] Ethylenethiourea has no radioprotective activity, but, after the introduction of methyl groups both into the hydrocarbon chain and at the nitrogen atom, compounds with an appreciable RPE are produced (30–40% protection) [compounds (CXXXII)].[66]

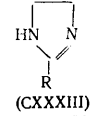


(CXXXI)
R, R′=H, Me; R″=Ar

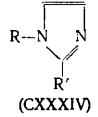


(CXXXII)
R=H, Me; R′, R″=H, Alk, Ar, R′, R″=alkylene

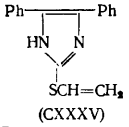
A deeper investigation of the RPE of imidazole and Naphthysin has been continued[113,115] together with the search for new radioprotectants among imidazoline and imidazole derivatives. In contrast to imidazolidine derivatives, 2-phenylimidazoline and its benzyl analogue (CXXXIIIa) proved to be inactive, while 2-imidazolidinethione (CXXXIIIb) protected 70–80% of the irradiated animals.[150] On passing to imidazoles, the 2-phenyl derivative (CXXXIV) again proved to be active.[150] Mono- and di-alkylimidazoles (CXXXIV) had a high RPE in experiments on mice,[150] while 4,5-diarylimidazolyl vinyl sulphides (CXXXV) proved to be relatively ineffective.[151]



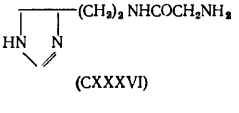
(CXXXIII)
a) R=Ph, $PhCH_2$;
b) R=OH, SH



(CXXXIV)
R=Alk, H; R′=H, Me, Ph



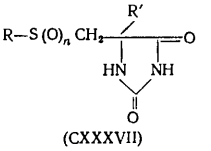
(CXXXV)
R=H, $CH=CH_2$



(CXXXVI)

A high radioprotective activity is observed after the subcutaneous administration of glycylhistamine (CXXXVI) to mice 24 h before irradiation and after intra-peritoneal administration 30 min before irradiation.[152] The substance administered intra-peritoneally becomes inactive after 24 h.

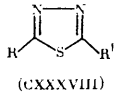
Interesting results have been obtained in the study of thiomethyl derivatives of hydantoins (CXXXVII); thus 5-propyl- and 5-allylthiomethyl-5-methylhydantoins (CXXXVIIa) are four times superior to cystine in terms of the test based on the survival of irradiated mice and by a factor of 2 in terms of the duration of their activity.[89,153] The replacement of the methyl group by hydrogen or the oxidation of sulphide sulphur to sulphoxide sulphur fully abolish the protecting activity of compounds (CXXXVII, b and c).[89,153]



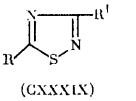
(CXXXVII)
a) R=H, Pr, $CH_2CH=CH$; R′=Me, $n=0$,
b) R=$CH_2CH=CH$; R′=Me; $n=1$,
c) R=$CH_2CH=CH$; R′=H; $n=0$.

Familiar medicinal preparations derived from pyrazolone (antipyrine, amidopyrine, and analgin[154,155]) as well as 1-heterylpyrazolones and 1-heterylpyrazoles,[148,149] possess weak protecting properties.

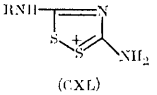
It has been shown[75] that, in the presence of the amino- and mercapto-groups in the molecules of 1,3,4-thiadiazole (CXXXVIII) and 1,2,4-thiadiazole (CXXXIX), the level of protection in mice does not exceed 30%. It has been found[156] that the 5-amino-3-arylamino-1,2,4-dithiazolium salts (CXL) exhibit a moderate protecting activity, the presence of the methoxy-group in the benzene ring tending to increase the activity.



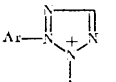
(CXXXVIII)
R = NR''_2; R′ = H, Me, SH, SMe



(CXXXIX)



(CXL)
R = H, Ar



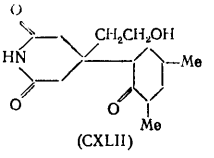
(CXLI)

The protecting effects of 5-mercaptomethyl-1,2,4-triazolin-3-one and 5-mercaptomethyl-1,2,4-triazoline-3-thione as well as the 2,5-diphenyl-1-phenylamino-1,3,4-triazolium salt are weak.[143]

Substances with a pronounced radioprotective activity have not been found among 5-substituted tetrazoles;[11] the water-soluble di- and tri-aryltetrazolium quaternary salts (CXLI), some of which, for example, compound (CXLI, R = Ar = Ph, X = Cl), protect up to 60% of mice irradiated with a lethal dose, are more promising in this respect.[157,158]

Thus highly effective radioprotectants belonging to the series of aryl derivatives of oxazolidines, thiazolidines, imidazolines, and thiomethylhydantoins have been found among five-membered heterocyclic compounds.

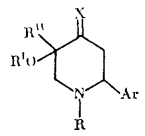
The search for radioprotectants among six-membered aromatic and non-aromatic heterocycles was less successful. Thus 3-hydroxy-2-methyl-4-pyrone (maketol)[159] does not protect irradiated mice.



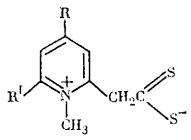
(CXLII)

Cycloheximide (CXLII) is of interest.[160] In experiments on rats it did not show a radioprotective activity when administered intra-abdominally directly before irradiation, but, when introduced in a dose of 2 mg kg^{-1} 6 and 12 h before irradiation, it effectively protected the skin and radiosensitive tissue. This compound is particularly attractive because it protects selectively normal tissues but not tumours.

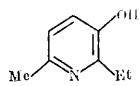
The structures of the piperidines and pyridines which have been investigated as potential radioprotectants but showed a low protecting activity or none at all are presented below:



R = Me, $PhCH_2$;
R^I = H, Ac; R^{II} = H, Me;
X = O, HOH (Ref.161)



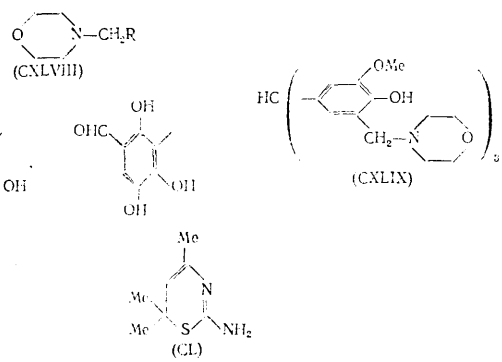
R = H, Me;
R^I = H, CH_2CSSNa (Ref.162)



(Ref.163)

Pyridinecarboxylic acids and their derivatives have been proposed as radioprotectants.[15] Nicotine bitartrate increases the lifespan of both young and old irradiated rats;[164] the possibility of using it in X-ray therapy is being considered.

Among six-membered heterocyclic compounds containing two heteroatoms, the Mannich bases (CXLVIII)[165] and (CXLIX),[166] which contain morpholine in their composition, exhibit a pronounced RPE. Thiomorpholine derivatives have been proposed as radioprotectants.[167,168]



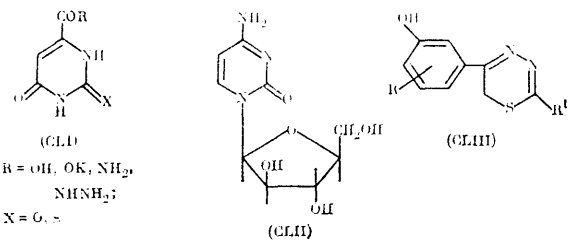
(CXLVIII)

(CXLIX)

(CL)

In the series of six-membered heterocyclic compounds with two heteroatoms, a pronounced antiradiation activity has been discovered only for 2-amino-4,6,6-trimethyl-1,3-thiazine (CL).[169]

A low level of protection against radiation or its total absence have been noted in a series of tetrahydro-derivatives of 2-amino- and 2-mercapto-1,3-oxazines[170] and the corresponding 1,3-thiazine[170,171] and pyrimidine[171] derivatives, the 2-thiones of hexa- and tetra-hydropyrimidines,[53,172] and also certain sulphur-containing derivatives of pyrimidine[135,162,173] and 2-amino-5-bromo-4-hydroxy-6-phenylpyrimidine.[39]



(CLI)

R = OH, OK, NH_2, $NHNH_2$;
X = O, S

(CLII)

(CLIII)

Two groups of investigators observed independently the high RPE of orotic acid and some of its derivatives (CLI).[174,177]

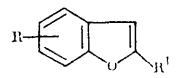
The familiar cytostatic compound cytosine arabinoside (CLII) does not protect mice when administered intra-abdominally 15–60 min before irradiation, but, when it is administered 48–72 h prior to radiation, the survival rate of mice irradiated with a lethal dose is 90%.[178]

A pronounced radioprotective effect has been observed for certain derivatives of 2-methylmercapto-1,3,4-thiadiazine (CLIII).[146] *sym*-Diphenyltetrazine and its 1,2-dihydro-analogue proved to be inactive.[143]

Thus, among six-membered heterocyclic compounds, derivatives of orotic acid and cytosine arabinoside are of greatest interest.

Among heterocyclic compounds investigated as potential radioprotectants, condensed systems and in the first place benzoheterocycles occupy a notable place.

2-Acetyl-6-methoxybenzofuran exhibits the highest RPE (70% survival rate) among the 14 benzofurans (CLIV) synthesised.[179]



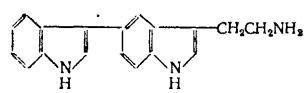
(CLIV)

R = H, OMe; R^I = H, CHO, Ac, CN, COOEt

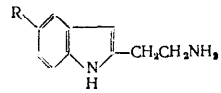
Indole derivatives are important among condensed heterocycles. The search for radioprotective agents in this series of compounds has been conducted mainly in two directions, i.e. via the modification of the tryptamine molecule (in the side chain or in the benzene ring) and via the synthesis of compounds with a non-tryptamine structure.

It has been shown[180] that tryptamine containing the indole substituent in the 5-position, as in compound (CLV), is superior in its radioprotective activity to the initial tryptamine but is inferior to mexamine.

5-Substituted isotryptamines (CLVI) proved to be weakly active.[181]

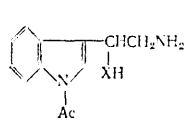


(CLV)

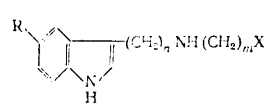


(CLVI)
R=H, Me,Cl, OH

Much attention has been devoted to the synthesis and investigation as possible radioprotectants of sulphur-containing derivatives of tryptamine and serotonin.[182–187] They are considered here and not in the previous Sections, since their indole structure in all probability plays the main role in their radioprotective activity. The synthesis of β-mercaptoethylamine and its *S*-functional derivatives (the sulphide, disulphide, sulphonate, and thiosulphate) with the indole substituent at the carbon atom [compound (CLVII)] did not lead to compounds with an appreciable radioprotective activity with the exception of compound (CLVII, R = H), which exhibits an RPE somewhat superior to that of tryptamine. A series of compounds in which the hydrogen atom in the amino-group of tryptamine or mexamine has been substituted by mercaptoalkyl groups [compounds (CLVIII)] have been synthesised.[183,184]



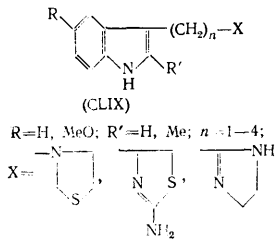
(CLVII)
X = SH, SO_3H, SSO_3H



(CLVIII)
R = H, MeO; n = 1, 4; m = 2, 3;
X = SH, SSO_3H, SPO_2H_2, $NHCH_2CH_2SH$

However, none of them has advantages as a radioprotectant relative to the initial unsubstituted amines. Analogous results have been obtained for 3-heterylalkyl-indoles and their 5-methoxy-derivatives (CLIX).[184,186]

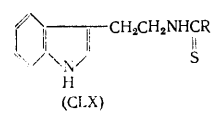
Thioamides containing the tryptamine residue (CLX) exhibt a high RPE.[185]



(CLIX)

R=H, MeO; R′=H, Me; n = 1—4;

X =

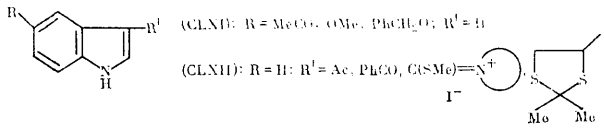


(CLX)

R=Me, Ph, $PhCH_2$

It has been shown[188] that the RPE of a series of 3-indolylalkylamines is correlated with the electron-donating activity calculated by quantum-mechanical methods.

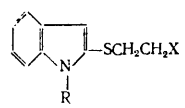
Attention has been given to indole derivatives without the aminoethyl group in the 3-position. Among a large number of 5-alkoxy- and 5-acetyl-substituted compounds (CLXI) as well as 3-carbonyl derivatives of indole (CLXII), substances with a moderate protecting activity have been discovered.[189] The absence of a pronounced radioprotective activity has been demonstrated for a series of 2-amino- and 4-, 5-, and 6-aminoethyl-indoles.[185,190]



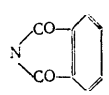
(CLXI): R = MeO, OMe, $PhCH_2O$; R′ = H

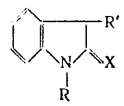
(CLXII): R = H; R′ = Ac, PhCO, C(SMe)=N⁺ I⁻

Indoles containing the mercaptoethyl functional group in the 2-position of the ring, as in compound (CLXIII),[185] exhibit a moderate RPE. Among indolinones, only the thio-derivative (CLXIV) shows a moderate radioprotective activity.[185]



(CLXIII)

X = NH_2, 

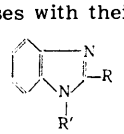


(CLXIV)

R=H, Me; R′=CH_2CN, CH(CN)COOH, $CH_2CH_2NH_2$; X=O, S

The search for radioprotective substances among derivatives of 2-aminobenzothiazole did not lead to compounds with an appreciable radioprotective activity.[147,169,191]

Certain other bicyclic heterocycles have been shown to exhibit an antiradiation activity. It has been stated[150,192] that a series of 2-alkyl- and 2-arylalkylbenzimidazoles (CLXV) exhibit a fairly high protecting activity in mice, which depends on the degree of lipophilicity of the molecule. The ethyl and *p*-chloro-α-hydroxybenzyl substituents [compounds (CLXV, a and b)] proved to be optimal; it is of interest that the toxic *o*-chloro-analogue shows no radioprotective activity.[150] It has been found that the toxicity of the compounds increases with their activity.



(CLXV)

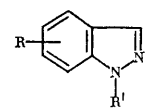
R=Alk, Ar, aryl alkyl;

R′=H

a) R=Et, b) R=

On the other hand, no appreciable protective activity has been observed for a whole series of benzimidazole derivatives with unsaturated and sulphur-containing substituents[151] and also *NN′*-dimethylbenzimidazolines and benzimidazolium salts.[79]

Interesting results have been obtained by a group of French investigators in a study of 23 compounds of the indazole series [compounds (CLXVI)].[193] They discovered that 6-nitroindazole (CLXVIa), administered in a dose corresponding to one half of LD_{50}, protects up to 90% of mice when administered intra-peritoneally 10 min before irradiation, while the 7-nitro- and 1-(*p*-chlorobenzoyl)-5-nitro-derivatives (CLXVI, b and c) ensured 70—80% protection of the animals when administered in a dose corresponding to one quarter of LD_{50}.

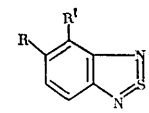


(CLXVI)

a) R = 6-NO_2, R′ = H

b) R = 7-NO_2, R′ = H

c) R = 5-NO_2; R′ = *n*-ClC_6H_4CO



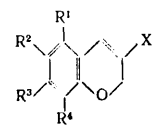
(CLXVII)

R=H; R′ = OH, NH_2, MeNH, Me_2N;

R = R′ = NH_2

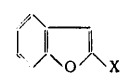
Extensive studies designed to find radioprotectants among benzo-2,1,3-thiadiazoles (CLXVII)—synthetic substitutes for a group of vitamins K [12,194–199]—made it possible to discover compounds with a pronounced antiradiation activity. These are in the first place the 4-hydroxy-, 4-amino-, 4-methylamino-, 4-dimethylamino-, and 4,5-diamino-derivatives.

Among the large group of 2*H*-chromenes (CLXVIII), substances have been found with a high radioprotective activity; the results for some of these are listed in Table 4.[179–200] The study of the comparative RPE of 2*H*-chromenes (CLXVIII) and benzofurans (CLXIX) containing identical substituents showed that the former have a more pronounced protective activity.



(CLXVIII)

X = CHO, Ac, CN, COOEt



(CLXIX)

Table 4. The radioprotective activity of compound (CLXVIII)[179] (intra-peritoneal administration to mice, 900 R γ-irradiation).

R¹	R²	R³	R⁴	X	LD_{50}, mg kg⁻¹	% protection		I
						for MTD*	for 1/4 LD_{50} dose	
H	H	OMe	H	CHO	600	60	50	6
H	H	H	H	MeCO	1000	40	80	7.2
H	H	OMe	H	MeCO	1000	80	60	6.4
H	H	H	OMe	MeCO	1000	100	50	6
OMe	H	H	H	MeCO	1000	30	70	6.8

*MTD = maximum transferable dose.

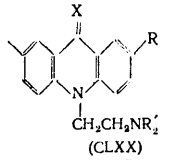
It has been reported[159,201–206] that many flavanoid compounds exhibit a pronounced radioprotective activity, but highly effective radioprotectants have not been discovered among them.

The vinyl derivatives of quinoline and its *N*-oxide,[207] derivatives of *N*-methylquinolinium and isoquinolinium containing the dithioacetic acid residue,[162] and *N*-acylaminoisoquinolinium salts[143] showed a low protecting effect in experiments on mice. Studies designed to find radioprotectants have been carried out among sulphenylamides and sulphides derived from quinoline and its *N*-oxide,[87,172,208-210] quinoxaline,[211] and 1,2-dihydrophthalazine,[212] but data on their activities are not quoted.

Apressin, which is a familiar medicinal preparation consisting of 1-hydrazinophthalazine,[155] protects 26.6% of the irradiated mice, while diazepam (7-chloro-1,3-dihydro-1-methyl-5-phenyl-1*H*-1,4-benzodiazepin-2-one) not only increases somewhat the survival rate of mice but also diminishes the toxicity of MEA.[213]

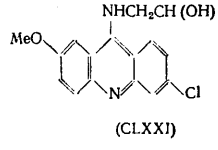
More complex benzoheterocyclic compounds have been subjected to radiobiological investigations to a much lesser extent.

Substances protecting more than 50% of the animals could not be found among *N*-substituted acridones (CLXX).[241] Acranil (CLXXI), an inductor of interferon, inhibits approximately the same effectiveness.[215]



(CLXX)

R=H, Cl, Br; R'=Me, Et; X=O, S



(CLXXI)

Thus certain indazole and chromene derivatives showed the highest radioprotective activity among benzoheterocyclic compounds.

In the series of condensed heterocyclic compounds, much attention has been devoted, as in the preceding period, to derivatives of purine and particularly adenosine. Substances with a moderate RPE have been discovered among sulphur-containing purine derivatives (CLXXII)[76] and (CLXXIII).[216] 2,6-Dimercaptonebularine has been described as a radioprotectant.[217] The absence of radioprotective activity has been noted for purine-8-thione and pyrido[2,3-*d*]imid-2-azolinethione.[135]

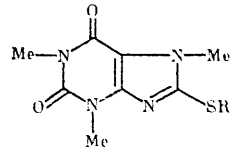
It has been found[218,219] that inosine (CLXXIV) exhibits a low protective activity, which is shown more distinctly when administered to small laboratory animals several days before irradiation. An increase in the survival rate of the irradiated mice has been observed after the prophylactic administration of certain 6-substituted adenosines.[220-222] The *p*-hydroxyphenylethyl and the indol-3-ylethyl derivatives (CLXXV) proved to be the most effective. It has been suggested[221] that the RPE of substances of this series is achieved via two pathways—via direct action at the cellular level and indirectly by virtue of the cardiovascular hypoxia induced by them. It has been shown[219,223] that the monophosphates of purine nucleosides exhibit a radioprotective activity and that their combination with ATP and sulphur-containing radioprotectors has a DRF = 2.[223] A review devoted to the mechanisms of the radioprotective activity of adenine compounds constitutes a kind of summary of studies on these lines.[224]

A clinical application of *S*-adenosylmethionine (CLXXVI) in X-ray therapy has been reported.[225]

The alkaloid emetin, which is an inhibitor of protein synthesis, exhibits a pronounced protecting activity when administered intra-peritoneally in a dose of 6.5 mg kg^{-1} 6–12 h before irradiation but not directly before irradiation.[160] The medicinal drug methotrexate also affords no protection when administered directly before irradiation, but provides 80% protection in mice when administered 24–48 h prior to irradiation.[178]

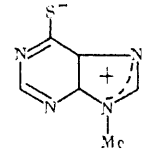
Derivatives of α-carboline proved to be ineffective.[197] The radioprotective properties of nalidixic acid (CLXXVII) have been reported.[226]

Detailed study of various types of synthetic porphyrins and their metal complexes showed[227-231] that among them there are compounds with a moderate RPE. This applies primarily to the *meso*-derivatives of aetioporphyrin-1 (CLXXVIII) and the tetra-alkyl ether-esters of haematoporphyrin (CLXXIX).

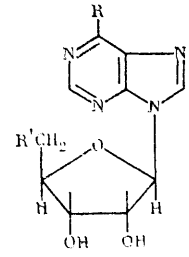


(CLXXII)

R = H, CH_2CH_2OH

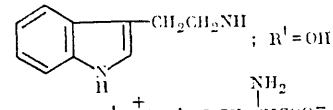


(CLXXIII)



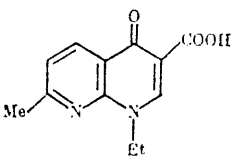
(CLXXIV): R = R' = OH

(CLXXV): R = *n*-$HOC_6H_4(CH_2)_2NH$,

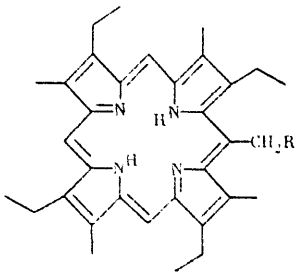


; R' = OH

(CLXXVI): R = NH_2, R' = $\overset{+}{S}(Me)CH_2CH_2\underset{NH_2}{\underset{|}{C}}HCOO^-$

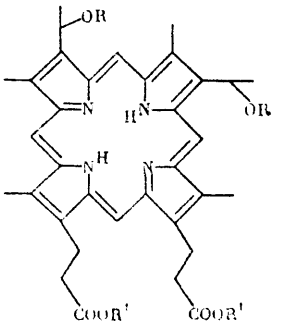


(CLXXVII)



(CLXXVIII)

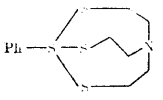
R = NHMe, NMe_2, MeO, $NH(CH_2)_2COOH$



(CLXXIX)

R = Alk, R' = H, Alk

It has been observed[242] that the acetylbenzoyl derivatives of the polycyclic alkaloid aconine is somewhat inferior in its radioprotective activity to MEA and AET. The silicon-containing heterocycle (CLXXX) has been proposed as a radioprotectant.[243]



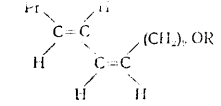
(CLXXX)

It follows from the data presented that substances with a high radioprotective activity have been discovered among heterocyclic compounds of different structure, which shows that further search for radioprotectants among them is promising.

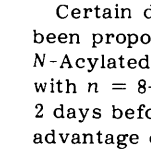
V. COMPOUNDS OF DIVERSE STRUCTURE

In this Section we shall consider aliphatic, aromatic, aliphatic-aromatic, and also certain phosphorus-containing compounds.

Isobombykol and its esters (CLXXXI) exhibit a high radioprotective activity.[244] Tests on a large number of patients showed that the prophylactic administration of *O*-alkylglycerols (CLXXXII)[245] diminishes the number of patients contracting radiation sickness in X-ray therapy.

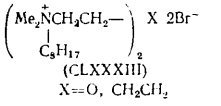


(CLXXXI)



(CLXXXII)

R = C_nH_{2n-1}; n = 7–16



(CLXXXIII)

X = O, CH_2CH_2

R"NHCHR'CHRCN

(CLXXXIV)

R, R', R" = H, Alk

Among other glycerol derivatives, 16 lipids and phospholipids of different structure have been studied, but effective protectors have not been found among them.[236] Nor have satisfactory antiradiation agents been found among different derivatives of amines, hydroxyamines, and diamines;[21] ethylenediamine[21] and quaternary salts of the type of (CLXXXIII),[10] which exhibit a pronounced RPE, are exceptions.

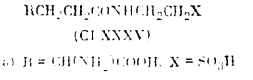
When administered in a dose of 30 mg kg^{-1} to mice, acetyl-β-methylcholine has a DRF = 1.27.[237]

The radioprotecting activity of β-aminonitriles (CLXXXIV) has been reported.[238,239]

Aminoacid derivatives continued to attract the attention of investigators. In particular, it has been shown[240] that potassium and magnesium aspartates administered to mice with food increase their survival rate and stimulate cell proliferation and differentiation in the thymus, spleen, and bone marrow.

Among the series of aminoacid protease inhibitors, only antipain increases somewhat the survival rate of mice.[24]

In recent years careful studies have been made of γ-*L*-glutamyltaurine (litoralon) (CLXXXVa), which was isolated from natural sources and subsequently synthesised and which exhibits a vitamin A-like activity.[246–250] This virtually non-toxic compound ensures a 50% survival rate of animals when introduced intra-peritoneally into mice in a dose of 100 mg kg^{-1} 4 days before irradiation. γ-Aminobutyryltaurine and its phosphorus analogue (CLXXXV, b and c) exhibit an analogous activity.[246–248]

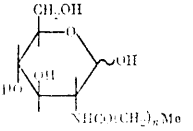


(CLXXXV)

a) R = $CH(NH_2)COOH$, X = SO_3H

b) R = CH_2NH_2, X = SO_3H

c) R = CH_2NH_2, X = $PO(OH)_2$



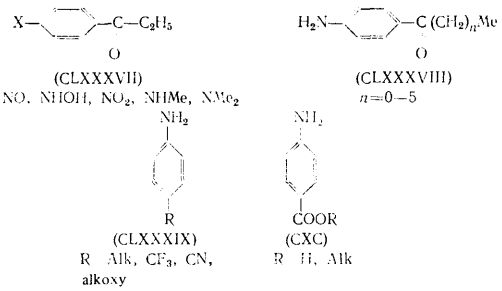
(CLXXXVI)

Certain disacharride derivatives with a low toxicity have been proposed as radioprotectants, but their RPE is low.[251,252] *N*-Acylated D-glucosamines (CLXXXVI), particularly those with *n* = 8–12, administered to mice in a dose of 0.05 mg kg^{-1} 2 days before irradiation, exhibit a high RPE.[253,254] A disadvantage of these substances is that they are virtually insoluble in water.

Thus aminoacid derivatives and, in particular litoralon, proved to be the most interesting among aliphatic compounds.

Since the 1950's, attempts have been made to employ antioxidants to protect the organism against the effects of radiation. During this period, studies have also been made of phenolic antioxidants used in the food industry, in particular of 2,6-di(t-butyl)-4-methylphenol,[255,256] but the degree of protection proved to be low.

Studies have continued on the radioprotective properties of derivatives and analogues of *p*-aminopropiophenone (CLXXXVII).[257] The influence of substituents on the RPE of compounds (CLXXXVII)–(CXC) has been investigated and it has been found that the aniline derivatives (CLXXXVIII, *n* = 3 and 4), (CLXXXIX, R = CF_3 or CN), and (CXC, R = Me or Et) have a somewhat higher activity than the parent *p*-aminopropiophenone.



(CLXXXVII)
X = NH_2 (a), NO, NHOH, NO_2, NHMe, NMe_2

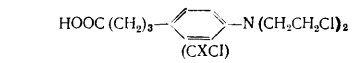
(CLXXXVIII)
n=0–5

(CLXXXIX)
R = Alk, CF_3, CN, alkoxy

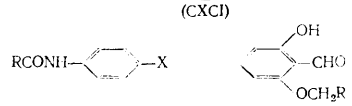
(CXC)
R = H, Alk

When administered in a dose of 12 mg kg^{-1} 72 h before irradiation, chlorambucil (CXCI) ensures a 65% survival rate of mice.[178]

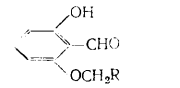
The anilides (CXCII) investigated proved to be relatively ineffective.[258,259]



(CXCI)



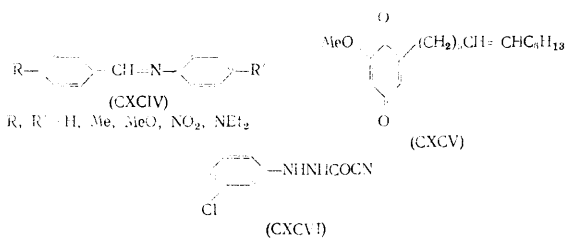
(CXCII)
R = Me, X = OH;
R = 2-OH-3-$NO_2C_6H_3$, X = Cl



(CXCIII)
R = Ar, CH_2CH_2R'
R' = H, Alk, CH_2COOH

The ethers of 2,6-dihydroxybenzaldehyde (CXCIII) have been proposed as radioprotectants.[260]

The radioprotective activity of a series of azomethines (CXCIV) has been investigated.[261] They exhibited only a weak antiradiation activity; a semiempirical calculation by the Hückel LCAO-MO method yielded a satisfactory correlation between the electron-donating properties of the compounds and the RPE.[261] The azomethines based on trihydroxybenzaldehydes proved to be more effective:



(CXCIV)
R, R' = H, Me, MeO, NO_2, NEt_2

(CXCV)

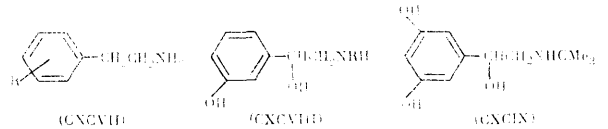
(CXCVI)

Among quinone derivatives, irisquinone (CXCV) has been proposed as a radioprotectant.[263]

The studies on organic derivatives of hydrazines have been continued: the data for the RPE of (3-chlorophenyl)hydrazino-oxoacetonitrile (CXCVI), which is an energy metabolism inhibitor, are contradictory,[264,265] while the medicinal preparation phelazine(2-phenylethylhydrazine) has a low activity.[155]

Considerable attention has been devoted during the period under consideration to phenylethylamine derivatives (CXCVIIa). Among compounds unsubstituted in the benzene ring, 2-amino-1-phenylethanol is the most active.[21,31]

More than 30 *o*-, *m*-, and *p*-hydroxy and *o*-, *m*-, and *p*-alkoxy-phenylethylamines (CXCVII) have been investigated, but no substances have been discovered among them which would increase the survival rate of the irradiated mice by more than 40%.[266] The replacement of the amino-group by the amido-, carbamido- and hydantoin groups decreased the toxicity but did not increase the RPE.[267]



(CXCVII)
R = H (a), OH, OAlk

(CXCVIII)
a) R = Me
b) R = Et

(CXCIX)

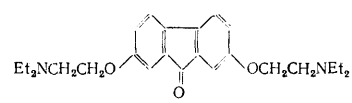
The introduction of the hydroxy-group in the β-position of *m*-hydroxyphenylethylalkylamine increases sharply the radioprotecting activity.[21,268–272] The *N*-methyl derivative (mezaton) and also the *N*-ethyl derivative (phetanol) [compounds (CXCVIII, a and b)] (25–50 mmol kg^{-1}) exhibit a stable RPE combined with a low toxicity (LD_{50} = 4.8 mmol kg^{-1}) when administered to mice subcutaneously (s/c) and intra-peritoneally. It has been shown[268,269] that the ED_{50} for the laevorotatory *S*-isomer of mezaton (CXCVIIIa) is lower almost by a factor of 2 than for the racemate (8.3 and 13 mol kg^{-1} respectively). It has been found that the *ortho*- and specially the *para*-hydroxy analogues of compound (CXCVIIIa) are less active.[269,272] The level of protection is reduced after the introduction of an additional hydroxy-group into the molecule of compound (CXCVIIIa) in the 4- or 6-position of the benzene ring.[269,270] The replacement of hydrogen in the amino-group by more bulky substituents, for example the adamantyl[269] or carbamido-groups,[267] leads to the loss of the RPE.

At the same time, the use of the β-sympathomimetic compound terbutaline (CXCIX) as a radioprotectant in the X-radiotherapy of tumours has been mentioned.[273]

Esterification of the phenolic hydroxyl or its substitution by the toluene-*p*-sulphonamide residue in compound (CXVIIIb) lowers the RPE.[269] 2-Amino-1-β-naphthylethanol proved to be inactive.[182]

Thus derivatives of arylalkanolamines are not inferior to aminothiols and indolylalkylamines as regards their RPE, being actually superior to them in terms of the width of their activity spectrum and the low optimum effective dose required,[268] but they suffer from the disadvantage that they give rise to a sharp and prolonged increase in blood pressure.[270]

The mechanism of the protection afforded by these compounds has not been ultimately elucidated. There exist convincing data showing that their action is associated with induced circulatory hypoxia,[31,270,271] but experimental data such as the lack of a decrease of the partial O_2 pressure in the liver and spleen when radioprotective doses of mezaton are used,[269] the presence of a protecting effect at the cellular level,[274,275] and the concentration-dependent influence of adrenolytic compounds on RPE[276,277] show that protection by these compounds can be achieved by their direct action on the cells. The radioprotective activity of sympathomimetic compounds is apparently realised via both a pharmacological pathway (indirectly) and at the cellular level; depending on the structure of the radioprotectant, the relative contributions by these pathways can vary.



(CC)

Tilorone (CC), which is a familiar interferon inductor, gives rise to a cyclic type of enhancement of the resistance of animals to radiation; thus, when administered to mice intra-peritoneally 15–30 min before irradiation, it gives rise to a pronounced RPE, after 3 h it is completely ineffective, and after 6 h its protection again reaches the initial

level. Satisfactory results have been obtained when compound (CC) was administered 2–3 days before irradiation.[215,273]

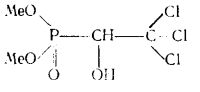
Steroids with a wide variety of structures have been used to increase the resistance of animals to radiation (see, for example, Refs.178, 279–285), but effective radioprotectants have not been discovered among them and furthermore these compounds were frequently administered to animals repeatedly over a fairly long period.

Various vitamins continue to attract the attention of radiobiologists but their protecting effect does not as a rule exceed an amount corresponding to a 30–40% survival rate.[286–292]

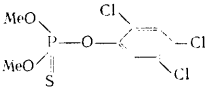
The results of studies of the radioprotective effect of vitamin K (ubiquinones) on mice merit attention. They proved effective when administered intra-peritoneally 10 h before irradiation.[292]

The demonstration of a high DRF in experiments on rabbit erythrocytes on treatment with riboflavin (DRF = 4.0), vitamin B_{12} (DRF = 3.6), and cytochrome *c* (DRF = 4.7) is also noteworthy.[291]

It has been found that penicillin exhibits a low radioprotective effect.[293]



(CCI)



(CCII)

The radioprotective activity of the organophosphorus compounds chlorophos (CCI) and trichlorometaphos (CCII) has been investigated in detail. When administered intra-peritoneally 3 h before irradiation, they afford protection to rats (DRF = 1.18 and 1.42 respectivcly).[294–299] These substances show a higher RPE when combined with dianabol and MEA.[297]

Thus, among aromatic and other compounds examined above, derivatives of phenylalkanolamines, which exhibit a high RPE and a broad therapeutic spectrum, have attracted attention.

Summarising, certain conclusions can be drawn. The number of publications devoted to the search for prophylactic radioprotective agents has increased somewhat, but the number of substances investigated (per annum) diminished somewhat, which applies in the first place to compounds with the aminothiol structure. A new class of highly effective radioprotectants, namely derivatives of arylalkanolamines, has been discovered. The relative contribution of heterocyclic compounds as potential radioprotective agents has greatly increased. It has been shown that thiazolidine derivatives are not unique among heterocyclic compounds as appeared to be the case previously; dithiolans and oxazolidines possess approximately the same activity. Other highly effective compounds, for example, chromenes and orotic acid derivatives, have been discovered.

For the first time, it has become possible to speak with confidence of the possibility of the practical application of radioprotectants. This has been confirmed by clinical studies on several preparations simultaneously, namely gammaphos, meprin, 5-thio-D-glucose, and terbutaline, in the prophylactic treatment designed to afford protection against radiation damage in cancer X-ray therapy.

A particularly vigorous search for new radioprotectants is to be expected in the next few years among heterocyclic compounds, arylalkanolamines, and aminothiol derivatives containing functional groups. This will be assisted by the data obtained in recent years demonstrating high RPE values for certain substances and data concerning the relation between structure and activity in various series of organic compounds.

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During the preparation of the manuscript for the press, several communications concerned with the search for radioprotective substances were published. The salts of adenosine 5'-monophosphate with MEA and cystamine have been investigated as radioprotectors;[300–303] *N*-adamantoylmercaptoethylamine proved to be relatively inactive.[304] Among the *S*-2-thiazoline[305] and *S*-2-furfuryl[306] derivatives of MEA, the latter showed a high RPE; the replacement of the amino-group by the amidino- or guanidino-group does not increase the activity.[306] Effective substances in the series of *N*-adamantyl derivatives of gammaphos and its analogues have not been discovered.[304] It has been found that, among derivatives of compounds (XXXV) and (XLVI) substituted at the nitrogen atom by aryloxyalkyl and arylalkyl groups, the highest activity is shown by *S*-2-[4-(5-methoxy-3-methylphenoxy)butylamino] ethylthiosulphuric acid.[307]

The preparation adeturon described above has been recommended for clinical tests in X-radiotherapy.[301,303,308] The adamantyl and adamantoyl derivatives of AET proved to be relatively inactive.[304] In contrast to the data recorded above concerning the relation between structure and activity, a correlation has been reported between the period of the radioprotective activity of 2-phenyl- and 2-*m*-bromophenyl-thiazolidines and their metabolism.[309] It has been shown that halogenoalkylisothiuronium salts exhibit a moderate RPE.[310]

The results of studies of the radioprotecting activity of sodium diethyldithiocarbamate have attracted attention: following its intra-peritoneal administration to mice 30 and 120 min before irradiation in a dose of 1000 mg kg^{-1}, the DRF = 1.5–1.6 was attained (for a dose of 335 mg kg^{-1} of the same substance, Bacg et al.[311] achieved 40% protection); sodium diethyldithiocarbamate has been recommended for clinical tests in X-ray therapy.[312–314]

Highly effective radioprotectors have been found among nitrogen-containing aromatic heterocyclic compounds with the mercapto-group in the side chain. The highest activity is shown by 2-mercaptomethylpyridine and the corresponding phosphorothioate (the *N*-oxides and 2-pyrazinylmethylphosphorothioic acid are somewhat inferior to them) as well as all the mercaptopyridine isomers.[315]

The radioprotective properties of alkyl 2-furyl and alkyl 2-pyranyl sulphides have been investigated.[316] Effective radioprotectants have not been discovered among pyridazine and pyridazine-3,6-dione derivatives.[317] Salts of mexamine with adenosine 5'-phosphates, which are more active than mexamine itself, have been obtained and investigated.[318] It has been shown that 1-β-hydroxyethyl-5-nitro-2-phenacylthiobenzimidazole[319] and certain xanthine, adenine, 8-aza-adenine, and 2-thio-8-aza-adenine derivatives which have been investigated[320] exhibit a weak protecting activity.

Among other bicyclic and tricyclic nitrogen-containing heterocycles of the quinoline[321] and azepine[322] series, derivatives of tetrahydro-1*H*-pyrido[3,2-*b*]azepine and tetrahydro-1*H*-pyrido[2,3-*b*]azepinone showed a high RPE.[322] The results of the primary selection from a series of synthetic porphyrins, namely derivatives of deuterioporphyrin (IX), mesoporphyrins IX and II, aetioporphyrins I and II, and coproporphyrin I (77 compounds in all), have been published.[323]

Interesting results have been obtained in the study of sulphur-containing sugars as radioprotectants.[324] Thus 6-thio-D-fructose (LD_{50} = 17.5 g kg^{-1}) administered intra-abdominally to rats in a dose of 500 mg kg^{-1} 30 or 120 min before irradiation ensured a 100% survival rate of the animals, whereas all the control animals died. The protective effect persists also if the compound is administered 6 h before irradiation.[324]

Among other substances of natural origin, radioprotecting activity has been observed for the tetrapeptide taftsin,[325] the polypeptide melittin,[326] and also the natural prostaglandin E_2 and its synthetic analogue 1,6-dimethylprostaglandin E_2.[327]

In the series of aromatic amines (*o*-toluidine derivatives), substances with radioprotective activity were not found.[322] A pronounced radioprotective activity of certain antihelminthic preparations has been reported,[328] namely 3,5-dibromo-*N*-[4-chloro-3-(4-chlorobenzoyl)phenyl]-2-hydroxybenzamide (tetalid [sic]) and 3,5-di-iodo-*N*-[4-chloro-3-(2,5-dimethylbenzoyl)phenyl]-2-hydroxybenzamide, but these data require confirmation, since the compounds were administered to the animals in solution in dimethyl sulphoxide, which itself exhibits a radioprotective activity.

As a supplement to the data discussed in the review, references may be made to studies devoted to the radioprotective effect of ubiquinones,[329] vitamin B_{12} and folic acid,[330] *N*-substituted 2-amino-1-*m*-hydroxyphenylethanols,[331] and the nitriles of cinnamic and hydrocinnamic acids.[332]

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Phosphorohalidites and Phosphoropseudohalidites in the Arbuzov Reaction with Halogen-containing Compounds

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The literature data on the reactions of phosphorohalidites and phosphoropseudohalidites with various halogen-containing compounds are surveyed and described systematically.
The bibliography includes 133 references.

CONTENTS

I.	Introduction	98
II.	Reactions of phosphoromonohalidites and phosphonomonohalidites with alkyl halides	98
III.	Reactions of phosphorodihalidites with alkyl halides	99
IV.	Phosphorohalidites in reactions with α-chloro- and α-bromo-alkyl isocyanates	99
V.	Phosphorohalidites in reactions with sulphenyl chlorides	100
VI.	Reactions of phosphorohalidites with *N*-chloro-compounds	101
VII.	Reactions of phosphoropseudohalidites with alkyl halides and *N*-chloro-compounds	101

I. INTRODUCTION

In his studies of the structure of phosphorous acid and its esters as long ago as the beginning of the present century, Arbuzov established that fully esterified phosphorous acids readily rearrange to esters of alkylphosphonic acids under the influence of alkyl halides.[1,2] Subsequently the reaction was extended to fully esterified phosphonous and phosphinous acids:

$$RR^1POR^2 + R^3X \rightarrow R^3P(O)RR^1 + R^2X\ .$$

In contrast to the full esters, phosphorohalidites and phosphonohalidites are less reactive and in most cases do not interact with alkyl halides under the usual conditions of the Arbuzov reaction. It appears that phosphorohalidites and phosphonohalidites because of their weak nucleophilic properties were made to undergo the Arbuzov rearrangement only after more than 50 years elapsed. Apart from its theoretical importance, this reaction is also of considerable practical interest, since with its aid it is possible to obtain extremely reactive derivatives of tetracoordinate quinquevalent phosphorus which may serve as the starting compounds in the synthesis of a wide variety of derivatives of phosphoric, phosphonic, and phosphinic acids. Several extensive reviews and review reports have been published[2-23] on reactions of the full esters, thioesters, and amidoesters of tervalent phosphorus acids with organic compounds both containing and not containing a halogen. In these publications there are only individual examples of reactions of phosphorohalidites and phosphoropseudohalidites. Certain aspects of the reactions of these phosphorus derivatives with halogen-containing compounds were described in somewhat greater detail in monographs,[24,25] in a report,[26] and in a review.[27] There are no complete reviews on the Arbuzov reaction involving phosphorohalidites and phosphoropseudohalidites.

We felt it of interest and timely to survey the available literature data on the reactions of these phosphorus derivatives with halogen-containing compounds.

II. REACTIONS OF PHOSPHOROMONOHALIDITES AND PHOSPHONOMONOHALIDITES WITH ALKYL HALIDES

It has been found during the last decades that the most reactive phosphorohalidites and phosphonohalidites are the monofluoro-derivatives: di-isopropyl phosphorofluoridite, alkyl methylphosphonofluoridites, and alkyl *NN*-dimethylphosphoramidofluoridites react with methyl iodide to form the products of the Arbuzov reaction:[28-30]

$$AlkOP(X)F + MeI \rightarrow MeP(O)(X)F + AlkI\ ;$$
$$X = AlkO,\ Me,\ Me_2N\ .$$

Dialkyl phosphorofluorofluoridites react analogously with carboxylic acid chlorides:[31]

$$(AlkO)_2PF + RCOCl \rightarrow RCOP(O)(OAlk)F + AlkCl\ .$$

It was established subsequently that compounds containing an activated carbon–halogen bond enter into the reaction with dialkyl phosphorohalidites under fairly mild conditions:

$$-\ddot{O}-\overset{|}{\underset{|}{C}}-Cl(Br, I),\quad -\ddot{S}-CH_2Cl\ =\ddot{N}-\overset{|}{\underset{|}{C}}-Cl(Br)$$

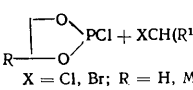
Alkyl α-chloroethyl ethers readily react with dialkyl phosphorochloridites to form alkyl α-alkoxyethylphosphonochloridates,[32,33] while alkyl -chloromethyl and alkyl αα-dichloromethyl ethers enter into the Arbuzov reaction only in the presence of a catalyst ($FeCl_3$):[34]

$$(RO)_2PX + R^1OCH(R^2)Cl \xrightarrow{(FeCl_3)} R^1OCH(R^2)P(O)(OR)X + RCl\ ;$$
$$X = Cl;\ R = Et,\ Bu,\ Am;\ R^1 = Et,\ Bu;\ R^2 = Me\ ;$$
$$X = Cl,\ F;\ R = Et;\ R^1 = Me,\ Et;\ R^2 = H,\ Cl\ .$$

The esters of chloro- and dichloro-acetic acids do not react with dialkyl phosphorohalidites. In contrast to them, the esters of alkoxychloroacetic acids do interact with dialkyl phosphorochloridites and phosphorofluoridites in the presence of catalysts (Lewis acids) and in their absence, while the esters of alkoxydichloroacetic acids react only in the presence of a catalyst:[34-37]

$$(EtO)_2PX + ClC(R^2)(COOR)OR^1 \xrightarrow{(FeCl_3)} R^1O(ROCO)C(R^2)P(O)(OEt)X + EtCl\ ;$$
$$X = Cl,\ F;\ R \text{ and } R^1 = Me,\ Et;\ R^2 = H,\ Cl\ .$$

When cyclic alkyl phosphorochloridites react with alkyl chloromethyl, alkyl bromomethyl, and alkyl dichloromethyl ethers, the Arbuzov reaction always proceeds with the rupture of the C–O bond at the unsubstituted carbon atom:[38-42]

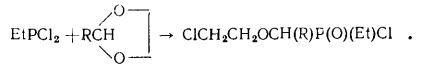


$$PCl + XCH(R^1)OR^2 \rightarrow R^2OCH(R^1)P(O)(Cl)OCH(R)CH_2Cl\ ;$$
$$X = Cl,\ Br;\ R = H,\ Me;\ R^1 = H,\ Cl;\ R^2 = Alk(C_1 - C_4)\ .$$

It has been shown[43-49] that the following are formed initially when phosphorus trichloride, alkyl phosphorodichloridites, and dichloroethyl- and dichlorophenylphosphines react with acetals, α-chloroethers and also dialkyl phosphorochloridites and alkyl ethyl(phenyl)phosphonochloridites among other tervalent phosphorous acid esters which enter into the Arbuzov reaction:

$$R^1CH(OR)_2 + R^2PCl_2 \rightarrow R^2(RO)PCl + R^1CHClOR \rightarrow ROCH(R^1)P(O)(R^2)Cl\ ;$$
$$PCl_3 + 2R^1CH(OR)_2 \rightarrow (RO)_2PCl + 2R^1CHClOR\ ;$$
$$(RO)_2PCl + R^1CHClOR \rightarrow ROCH(R^1)P(O)(OR)Cl\ ;$$
$$R = Alk;\ R^1 = H,\ Me;\ R^2 = AlkO,\ Et,\ Ph\ .$$

Dichloroethylphosphine reacts similarly with 2-alkyl-1,3-dioxolanes:[50]



$$EtPCl_2 + RCH(OCH_2CH_2O) \rightarrow ClCH_2CH_2OCH(R)P(O)(Et)Cl\ .$$

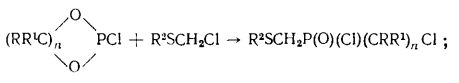
The reactions of dialkyl phosphorochloridites with acylals lead to the formation of α-chloroethers, which interact with the initial dialkyl phosphorochloridites:[51]

$$(RO)_2PCl + MeCH(OR^1)OCOMe \rightarrow (RO)_2POCOMe + MeCHClOR^1\ ;$$
$$(RO)_2PCl + MeCHClOR^1 \rightarrow R^1OCH(Me)P(O)(OR)Cl\ .$$

Alkylacetyl phosphorochloridites and acetyl phosphonochloridites, formed when phosphorodichloridites or dichlorophosphines are treated with acetic anhydride or an acetic acid acylal, react with α-chloroethers analogously to dialkyl phosphorochloridites and alkyl phosphonochloridites.[52-57] A reaction of the same type occurs between phosphorus trichloride and a mixture of acetic anhydride and its acetal:[58]

$$RPCl_2 + (MeCO)_2O \rightarrow RP(Cl)OCOMe \xrightarrow{MeCH(Cl)OR^1} R^1OCH(Me)P(O)(R)Cl\ ;$$
$$R = AlkO,\ Et,\ Ph\ .$$

The reaction of cyclic phosphorochloridites with alkyl chloromethyl sulphides has been patented:[59]



$$(RR^1C)_n(O_2)PCl + R^2SCH_2Cl \rightarrow R^2SCH_2P(O)(Cl)(CRR^1)_nCl\ ;$$
$$n = 2,\ 3;\ R \text{ and } R^1 = H,\ Me\ .$$

III. REACTIONS OF PHOSPHORODIHALIDITES WITH ALKYL HALIDES

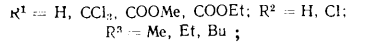
Arbuzov showed that neither methyl iodide nor benzyl chloride act upon the "Menshutkin acid chloride" ($MeOPCl_2$) even on heating at 200 °C for 12 h.[3] However, according to patent data,[60,61] the products of the Arbuzov rearrangement are formed on heating (in a sealed tube at 260–325 °C) methyl phosphorodichloridite with MeI, MeCl, or CCl_4 in the presence of catalysts ($FeCl_3$, ZnI_2, NiI_2, etc). Under milder conditions in the absence of a catalyst, methyl phosphorodichloridite reacts with allyl iodide[62] and ethyl phosphorodichloridite reacts with 4,5-methylenedioxy-2-propylbenzyl iodide.[63]

Methyl and ethyl phosphorodichloridites[64-70] and also butyl phosphorodifluoridite[69-71] enter into the Arbuzov reaction much more readily (than into the reaction with methyl iodide) on treatment with α-chloroalkyl ethers containing[69,70] or not containing[66-68,71] an electronegative alkoxycarbonyl group or three methyl groups at the α-carbon atom.

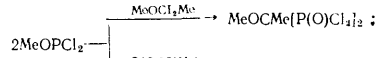
When alkyl phosphorodichloridites[71-73] and butyl phosphorodifluoridite[71,73] react with dichloromethyl methyl and di(chloromethyl) ethers[72] or with the alkyl esters of alkoxydichloroacetic acids,[71,73] only one chlorine atom is involved in the reaction even in the presence of a large excess of the phosphorodihalidite, while in the reaction of methyl phosphorodichloridite with di(α-chloroethyl) ether or αα-diiodoethyl methyl ether both halogen atoms are substituted:[27]

$$ROCR^1R^2Cl + R^3OPX_2 \rightarrow ROCR^1R^2P(O)X_2 + R^3Cl\ ;$$
$$X = Cl,\ F;\ R = Alk(C_1 - C_4),\ ClCH_2;$$

$$R^1 = H,\ CCl_3,\ COOMe,\ COOEt;\ R^2 = H,\ Cl;$$
$$R^3 = Me,\ Et,\ Bu\ ;$$



$$2MeOPCl_2 \xrightarrow{MeOCl_2Me} MeOCMe[P(O)Cl_2]_2\ ;$$



$$2MeOPCl_2 \xrightarrow{O(CHClMe)_2} O[CH(Me)P(O)Cl_2]_2\ .$$

The reaction of dialkyl formals with an excess of phosphorus trichloride in the presence of $ZnCl_2$ results in the formation of α-chloroethers and alkyl phosphorodichloridites, which react with one another via the mechanism of the Arbuzov reaction:[47,48,74]

$$PCl_3 + (RO)_2CH_2 \rightarrow ROPCl_2 + ROCH_2Cl \rightarrow ROCH_2P(O)Cl_2\ .$$

Alkyl chloromethyl and aryl chloromethyl sulphides react with alkyl phosphorodichloridites analogously to α-chloroethers:[75,76]

$$RSCH_2Cl + R^1OPCl_2 \xrightarrow{-R^1Cl} RSCH_2P(O)Cl_2\ ;$$
$$R = Et,\ Pr,\ iso\text{-}Pr,\ Bu,\ Ph\ .$$

IV. PHOSPHOROHALIDITES IN REACTIONS WITH α-CHLORO- AND α-BROMO-ALKYL ISOCYANATES

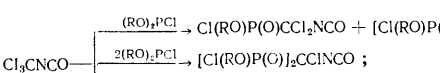
Dialkyl phosphorochloridites and dialkyl phosphorofluoridites undergo the Arbuzov rearrangement very readily on reaction with α-chloro- and α-bromo-alkyl isocyanates, forming α-alkoxychlorophosphonylalkyl and α-alkoxyfluorophosphonylalkyl isocyanates:[24,26,77-85]

$$(RO)_2PX + YCH(R^1)NCO \rightarrow X(RO)P(O)CH(R^1)NCO + RY\ ;$$
$$X = Cl,\ F;\ Y = Cl,\ Br;\ R = Et,\ iso\text{-}Pr;\ R^1 = H,\ Cl,\ Ph,\ BrCH_2,\ CCl_3\ .$$

The reaction of dichloromethyl isocyanate with two moles of dialkyl phosphorofluoridite produces bis(alkoxyfluorophosphonyl)methyl isocyanate:[26,80,81]

$$2(RO)_2PF + Cl_2CHNCO \rightarrow [F(RO)P(O)]_2CHNCO\ .$$

The reaction of trichloromethyl isocyanate with one mole of dialkyl phosphorochloridite affords a mixture of alkoxychlorophosphonyldichloromethyl and bis(alkoxychlorophosphonyl)chloromethyl isocyanates, while the reaction with two moles of the reagent gives rise to the bisphosphorylated isocyanate only. Whatever the proportions of trichloromethyl isocyanate and dialkyl phosphorofluoridite, it is possible to isolate only bis(alkoxyfluorophosphonyl)chloromethyl isocyanate:[26,86]



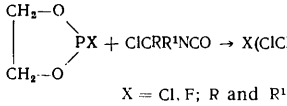
$$Cl_3CNCO \xrightarrow{(RO)_2PCl} Cl(RO)P(O)CCl_2NCO + [Cl(RO)P(O)]_2CClNCO\ ;$$
$$Cl_3CNCO \xrightarrow{2(RO)_2PCl} [Cl(RO)P(O)]_2CClNCO\ ;$$
$$Cl_3CNCO \xrightarrow[n=1,\ 2,\ 3]{n(RO)_2PF} [F(RO)P(O)]_2CClNCO\ .$$

Dialkyl phosphorochloridites react also with dichlorophosphonyl dichloromethyl isocyanate to form a mixed bisphosphorylated chloromethyl isocyanate:[26,86]

$$(RO)_2PCl + Cl_2P(O)CCl_2NCO \rightarrow Cl(RO)P(O)[Cl_2P(O)]CClNCO\ .$$

Cyclic phosphites (2-chloro- and 2-fluoro-phospholans) react with chloro-, dichloro-, and trichloro-methyl isocyanates via the mechanism of the Arbuzov rearrangement

involving ring opening and the formation of the corresponding β-chloroethoxychloro- and β-chloroethoxyfluorophosphonylalkyl isocyanates:[26,87]



$$X = Cl, F;\ R \text{ and } R^1 = H, Cl\ .$$

When alkyl phosphorodichloridites and phosphorodifluoridites react with α-chloro- or α-bromo-alkyl isocyanates, dichlorophosphonyl- and difluorophosphonyl-alkyl isocyanates are formed. The reaction proceeds only in the presence of Lewis acids as catalysts:[24,26,77-79,81-84,86,88-90]

$$R^2OPX_2 + YCRR^1NCO \rightarrow X_2P(O)CRR^1NCO\ ;$$
$$X = Cl, F;\ Y = Cl, Br;\ R = H;\ R^1 = H, Cl, CCl_3, CH_2Cl,;$$
$$CH_2Br, Ph \text{ or } R = R^1 = Cl\ .$$

α-Bromobenzyl isothiocyanate reacts with alkyl phosphorodichloridites and phosphorodifluoridites analogously to α-halogenoalkyl isocyanates:[91]

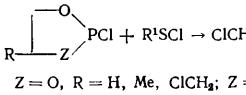
$$ROPX_2 + PhCHBrNCS \rightarrow X_2P(O)CH(Ph)NCS\ ;$$
$$X = Cl, F\ .$$

V. PHOSPHOROHALIDITES IN REACTIONS WITH SULPHENYL CHLORIDES

Dialkyl phosphorochloridites and phosphorofluoridites react very readily with alkane- and arene-sulphenyl chlorides via the mechanism of the Arbuzov rearrangement to form the alkyl and aryl esters of phosphorohalidothiolates:[25,92-95]

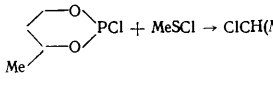
$$(RO)_2PX + R^1SCl \rightarrow R^1S(RO)P(O)X\ .$$

Five-membered cyclic phosphorochloridites, namely 2-chloro-1,3,2-dioxaphospholans, 2-chloro-1,2,3-oxathiaphospholans, and 2-chloro-1,3,2-oxazaphospholans, react with alkane- and arene-sulphenyl chlorides with ring opening at the C–O bond (at the unsubstituted carbon atom in 1,3,2-dioxaphospholans:[96-98]



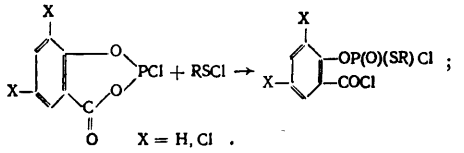
$$Z = O,\ R = H, Me, ClCH_2;\ Z = S, NAlk,\ R = H\ .$$

The C–O bond at the substituted carbon atom is ruptured in six-membered cyclic phosphorochloridites:[98]



When a mixture of an alkyl phosphorodichloridite and acetic anhydride or acetic acid is treated with alkane- and arene-sulphenyl chlorides, acetyl alkyl phosphorochloridites are apparently formed initially and undergo the Arbuzov rearrangement with formation of acetyl chloride.[99,100] The cyclic "salicyl phosphorochloridite" reacts similarly:[101]

$$ROPCl_2 + (MeCO)_2O \rightarrow RO(MeCOO)PCl \xrightarrow{R^1SCl} R^1S(RO)P(O)Cl\ ;$$



$$X = H, Cl\ .$$

Alkane- and arene-sulphenyl chlorides are more reactive than alkyl halides; they enter into the Arbuzov reaction with alkyl phosphorodichloridites and phosphorodifluoridites in the absence of catalysts:[93,94,102-108]

$$ROPX_2 + R^1SCl \rightarrow R^1SP(O)X_2\ .$$

The Arbuzov reaction probably proceeds also when a mixture of phosphorus trichloride and acetic anhydride is treated with alkane- and arene-sulphenyl chlorides:[100]

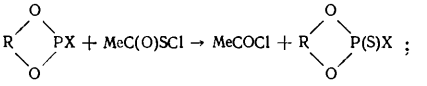
$$PCl_3 + (MeCO)_2O \rightarrow MeCOCl + MeCOOPCl_2 \xrightarrow{RSCl} RSP(O)Cl_2\ .$$

Selenyl chlorides react with alkyl phosphorodichloridites analogously to sulphenyl chlorides, but the reaction proceeds only in the presence of catalysts ($SbCl_5$, BCl_3):[108,109]

$$ROPCl_2 + CF_3SeCl \rightarrow CF_3SeP(O)Cl_2\ .$$

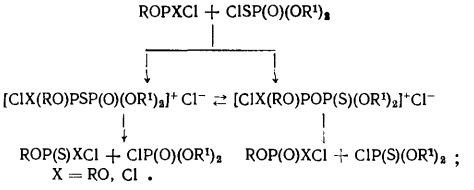
Acetyl-, dialkylphosphono-, and dialkylamino- or *N*-alkyl-*N*-(dialkyl phosphonoamino)-sulphenyl chlorides also react readily with dialkyl phosphorohalidites and alkyl phosphorodihalidites, but the products of the Arbuzov rearrangement are not formed.

Thus cyclic phosphorochloridites, phosphorobromidites, and phosphorofluoridites react with acetylsulphenyl chloride to form acetyl chloride and phosphorohalidothionates:[110-112]



$$R = -(CH_2)_2-,\ -CH_2CH_2CH(Me)-;\ X = Cl, Br, F\ .$$

When dialkyl phosphonosulphenyl chlorides are treated with dialkyl phosphorochloridites and alkyl phosphorodichloridites, either sulphur or oxygen is split off:[25,113]



$$X = RO, Cl\ .$$

Dialkyl phosphorochloridites and alkyl phosphorodichloridites react with dialkylamino- and *N*-methyl-*N*-dialkoxyphosphonylamino-sulphenyl chlorides in proportions of 2 : 1 to form an alkyl chloride, an alkyl phosphorodichloridate, or phosphoryl chloride and amides of phosphorothionic acids, while dialkyl phosphorofluoridites and alkyl phosphorodifluoridites are converted into mixtures of phosphorofluoridothionates and phosphoramidofluoridates. It has been suggested that the products of the Arbuzov rearrangement, namely alkoxyhalogenophosphonyl- or dihalogenophosphonyl-sulphenyl amides, are formed initially and then react in different ways with a second molecule of the corresponding phosphorohalidite:[25,114-118]

$$ROPXY + R^1R^2NSCl \rightarrow [XY(RO)PSNR^1R^2]^+Cl^- \rightarrow RCl + [XYP(O)SNR^1R^2]\ ;$$
$$X = Cl, F, OR;\ Y = Cl, F;\ R^1 = Me,\ R^2 = P(O)(OEt)_2 \text{ or } R^1 \text{ and } R^2 = Alk\ ;$$
$$[XClP(O)SNR^1R^2] + ROPXCl \rightarrow [XClP(O)SP(NR^1R^2)(OR)XI^+Cl^- \rightarrow$$
$$\rightarrow XP(O)Cl_2 + R^1R^2NP(S)(OR)X\ ;$$
$$X = Cl, OR\ ;$$
$$[XFP(O)SNR^1R^2] + ROPXF \rightarrow [XFP(O)S(NR^1R^2)P(OR)FX] \rightarrow XFP(O)NR^1R^2 + ROP(S)FX;$$
$$X = F, OR\ .$$

Dichloromethyleneiminosulphenyl chloride reacts with alkyl phosphorodichloridites analogously to dialkylaminosulphenyl chlorides:[119,120]

$$2ROPCl_2 + Cl_2C{=}NSCl \rightarrow Cl_2C{=}NP(S)(OR)Cl + POCl_3 + RCl\ .$$

VI. REACTIONS OF PHOSPHOROHALIDITES WITH *N*-CHLORO-COMPOUNDS

Dialkyl phosphorochloridites and phosphorofluoridites as well as alkyl phosphorodichloridites and phosphorodifluoridites react very readily with esters of *N*-chloroamidocarboxylic acids [*N*-chloroimidic acids? (Ed.of Translation)] via the mechanism of the Arbuzov reaction:[121]

$$ROPXY + R^1(R^2O)C{=}NCl \rightarrow R^1(R^2O)C{=}NP(O)XY ;$$
$$X = RO, Cl, F;\ Y = Cl, F;\ R^1 = Me, R^2O;\ R^2 = Me, Et .$$

The reactions of dialkyl phosphorochloridites with the esters of *N*-alkyl-*N*-chlorocarbamic acids also yield the products of the Arbuzov rearrangement:[122]

$$(RO)_2PCl + R^1OCON(R^2)Cl \rightarrow R^1OCON(R^2)P(O)(OR)Cl .$$

When phosphorus trichloride reacts with glycols and esters of *N*-alkyl-*N*-chlorocarbamic acids, the initial products are apparently cyclic phosphorochloridites, which then react with the *N*-chloro-compounds:[123]

$$PCl_3 + HOROH \rightarrow \text{cyclic } R(O)_2PCl \xrightarrow{R^1OCON(R^2)Cl} R^1OCON(R^2)P(O)(ORCl)Cl ;$$
$$R = (CH_2)_2,\ (CH_2)_3,\ CH(Me)CH(Me) .$$

Alkyl phosphorodichloridites react with the alkyl esters of *N*-alkyl-*N*-chlorocarbamic acids in the presence of the catalyst ($FeCl_3$):[124]

$$ROPCl_2 + R^1OCON(R^2)Cl \xrightarrow{FeCl_3} R^1OCON(R^2)P(O)Cl_2 .$$

When butyl phosphorodifluoridite is heated with *N*-chloro-*NN'*-dimethylbenzamidine, *N*-difluorophosphonyl-*NN'*-dimethylbenzamidine is obtained.[125]

VII. REACTIONS OF PHOSPHOROPSEUDOHALIDITES WITH ALKYL HALIDES AND *N*-CHLORO-COMPOUNDS

Dialkyl phosphorocyanidites enter into the Arbuzov reaction with alkyl iodides on prolonged heating in a sealed tube at 160 °C:[126]

$$(RO)_2PCN + R^1I \rightarrow R^1P(O)(OR)CN ;$$
$$R = Et, Pr;\ R^1 = Me, Et, Pr .$$

The esters of *N*-chlorimidocarboxylic acids [*N*-chloroimidic acids? (Ed.of Translation)] react with dialkyl phosphorocyanidites and alkyl phosphorodicyanidites in benzene:[121]

$$ROP(X)CN + R^1(R^2O)C{=}NCl \rightarrow R^1(R^2O)C{=}NP(O)(X)CN ;$$
$$X = RO, CN;\ R^1 = Me, R^2O;\ R^2 = Me, Et .$$

On prolonged refluxing, diethyl phosphoroisocyanatidite reacts with alkyl iodides via the mechanism of the Arbuzov rearrangement to form *O*-ethylalkylphosphonyl isocyanates:[127,128]

$$(EtO)_2PNCO + RI \rightarrow RP(O)(OEt)NCO ;$$
$$R = Me, Et, Bu, C_8H_{17} .$$

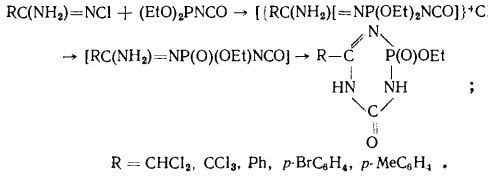
α-Chloroalkyl ethers react with diethyl phosphoroisocyanatidite much more readily than alkyl iodides, whilst αα-dichloroalkyl ethers react only in the presence of the catalyst ($FeCl_3$):[24,129]

$$(EtO)_2PNCO + ROCR^1R^2Cl \rightarrow ROCR^1R^2P(O)(OEt)NCO ;$$
$$R = Me, Et;\ R^1 = H, Cl;\ R^2 = H, COOMe, COOEt .$$

Ethyl phosphorodi-isocyanatidite reacts with α-chloro- and αα-dichloroalkyl ethers only in the presence of the catalyst:[129,130]

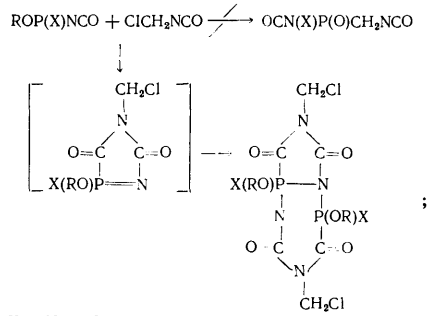
$$EtOP(NCO)_2 + ROCR^1R^2Cl \xrightarrow{FeCl_3} ROCR^1R^2P(O)(NCO)_2 ;$$
$$R = Me, Et;\ R^1 = H, Cl;\ R^2 = H, CCl_3, COOMe, COOEt .$$

The reactions of diethyl phosphoroisocyanatidite with *N*-chloroamidines yield the corresponding phosphonium salts, which readily split off ethyl chloride and are converted into *N*-(*O*-ethylisocyanatophosphonyl)amidines. The latter cyclise to 2-ethoxy-2,4-dioxo-6-R-2,3,4,5-tetrahydro-1,3,5,2-triazaphosphorinanes:[127,131]



$$RC(NH_2){=}NCl + (EtO)_2PNCO \rightarrow [\{RC(NH_2)[{=}NP(OEt)_2NCO]\}^+Cl^-] \rightarrow$$
$$\rightarrow [RC(NH_2){=}NP(O)(OEt)NCO] \rightarrow \text{cyclic } R(NH)_2C{=}NP(O)(OEt) ;$$
$$R = CHCl_2,\ CCl_3,\ Ph,\ p\text{-}BrC_6H_4,\ p\text{-}MeC_6H_4 .$$

When diethyl phosphoroisocyanatidite and alkyl phosphorodi-isocyanatidites are treated with chloromethyl and *p*-chloromethylphenyl isocyanates, it is not possible to obtain the products of the rearrangement—the reaction proceeds via a different pathway. The [3 + 2] -cycloaddition initially results in formation of a substituted 3,5-dioxo-Δ^1-1,4,2-diazaphospholine, which dimerises very readily to the tricyclic 1,3,2λ^5,4λ^5-diazadiphosphetidine:[24,132,133]



$$ROP(X)NCO + ClCH_2NCO \rightarrow OCN(X)P(O)CH_2NCO \rightarrow \text{cyclic } [X(RO)P{=}N]_2 ;$$
$$X = NCO,\ R = Me, Et, Pr, Bu \text{ or } X = RO = EtO .$$

It follows from the data presented in this review that a new development has arisen in recent years in the Arbuzov reaction, whose 80th anniversary occurs in 1985, consisting in the fact that phosphorohalidites, phosphoropseudohalidites, phosphonohalidites and phosphonopseudohalidites, which exhibit reduced nucleophilic properties, are also capable of undergoing the rearrangement on reaction with various halogen-containing electrophiles. The extension of the Arbuzov reaction to phosphorohalidites, phosphoropseudohalidites, phosphonohalidites, and phosphonopseudohalidites made it possible to obtain directly the mono- and di-halides and the mono- and di-isocyanates of tetracoordinate phosphorus acids, as well as their other highly reactive derivatives, which have found extensive applications in the synthesis of a wide variety of organophosphorus compounds possessing useful properties.

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The Mechanism of the Reaction of Hydrogen with the Metals of the Iron Sub-group

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The results of quantum-chemical studies of the mechanism of formation of the metal-hydrogen adsorption bond and the solution of hydrogen in group VIII metals, and the results of experimental studies of the chemisorption properties of metals of the iron sub-group with respect to hydrogen, have been reviewed. The experimentally observed regular features of the change in the bond strength and the concentration of different forms of chemisorbed hydrogen agree with the results of the quantum-chemical calculations.
The bibliography contains 111 references.

CONTENTS

I. Introduction 105
II. The nature of the metal-hydrogen adsorption bond 105
III. The solution of hydrogen in metals 110

I. INTRODUCTION

Extensive experimental and theoretical material has now been accumulated in the study of the adsorption of hydrogen on transition metals.[1-8] A number of problems related to the nature of the adsorption bond, the structure of the surface centres, etc. have not yet been resolved, however. The application of modern physical methods of study (low-energy electron diffraction (LEED), ultraviolet spectroscopy, energy-loss spectroscopy (ELS), etc.) and quantum-chemical methods to the study of the reaction of hydrogen with transition metals has made it possible to approach an understanding of the mechanism of the chemisorption of hydrogen and the relationship between the adsorbing power of metals and their electronic structure.

Recent studies illuminating the role of *d* and *sp* electrons in the adsorption of hydrogen, the influence of the structure of the active centre on the chemisorption of hydrogen, and various models of the dissociative chemisorption of hydrogen on 3*d* transition metals will be reviewed.

II. THE NATURE OF THE METAL HYDROGEN ADSORPTION BOND

1. The Role of *d* and *sp* Electrons in the Adsorption of Hydrogen on 3*d* Metals

In the first papers proposing models of the surface active centres in the chemisorption of hydrogen on transition metals,[6,9,10] it was assumed that the adsorption of hydrogen involves only *d* electrons, and that the directions in space and the splitting of the *d* orbitals with respect to energies are preserved for the surface atoms of the metal (Goodenough's model of the electronic structure of transition

metals[11] was used). It was shown that several types of chemisorption active centres may be formed on the (111), (110), and (100) crystallographic faces of single crystals of nickel and platinum as a result of the emergence of the corresponding e_g or t_{2g} orbitals on to the surface.

Modelling adsorption complexes in accordance with Goodenough's theory of the electronic structure of transition metals gives satisfactory correlations between the experimental and calculated values of the kinetic and thermodynamic parameters of adsorption. A large amount of data on the change in the electronic state of metal and hydrogen atoms during chemisorption, obtained in the last ten years using modern physical and quantum-chemical methods of study, however, indicate that not only the *d* orbitals, but also the *sp* orbitals, of transition metals are involved in the formation of the H–M bond.[12–28]

The principal results of the study of the adsorption of hydrogen on transition metals, obtained using cluster models of adsorption[12,13] and semi-empirical methods of calculation, taking account of the contribution of both the *d* and the *sp* orbitals of the metal to the formation of the H–M bond can be considered.

Calculations by the extended Hückel method (EHM) of the energy of adsorption of a hydrogen molecule on the cluster formed by two neighbouring atoms in a metal lattice (M = Cu, Ni) have shown that the interaction of the 1*s* orbitals of the hydrogen molecule with the $3d_{z^2}$ orbitals of Ni_2 leads to the activationless dissociation of the hydrogen molecule with the subsequent localisation of the H atoms on the $3d_{z^2}$ centres of of nickel; the 4*s* orbitals of nickel and copper can form bonds only with hydrogen atoms.[14]

The simultaneous participation of the 3*d*, 4*s*, and 4*p* electrons of the nickel atom in the chemisorption of atomic hydrogen with allowance for the influence of the nearest neighbouring metal atoms in the lattice has been examined by the EHM in Ref.15 (3*d* and 4*s* electrons) and in Refs.16 and 17 (3*d*, 4*s*, and 4*p* electrons). The adsorption was calculated for surface clusters consisting of 8, 9, or 10 nickel atoms, arranged in such a way that the metal atom interacting with hydrogen had the complete immediate environment corresponding to its position on the (100), (110), or (111) faces of a face-centred cubic (f.c.c.) lattice. The most satisfactory agreement between the calculated and experimentally determined values of the H–M bond energies (290 kJ $mole^{-1}$ [29]) was observed when the simultaneous contributions of both the 3*d* and the 4*s* surface states of the nickel atom were taken into account in the calculation.[15] The population of the $3d_{z^2}$ orbital of the nickel atom interacting directly with the hydrogen atom changed during adsorption from 1.904 to 0.972, and that of the 4*s* orbital from 0.468 to 0.368. The changes in the populations of the $3d_{x^2-y^2}$, $3d_{xy}$, $3d_{xz}$, and $3d_{yz}$ orbitals, and also the 4*p* orbitals of the given atom, and the 3*d* and 4*sp* orbitals of the metal atoms surrounding the active centre, were found to be slight for all types of cluster examined.[15–17]

The preferred participation of the 4*s* orbitals of Ni in bond formation with molecular forms of hydrogen has been demonstrated.[18] A semi-empirical MO LCAO calculation of the adsorption of a hydrogen molecule on a centre formed by two neighbouring nickel atoms (Ni–Ni bond length 2.49 Å), with allowance for the contribution to the bond of the 1*s* orbital of hydrogen and the $3d_{z^2}$ and 4*s* orbitals of the metal, on the energy surface of the dissociative chemisorption revealed three states corresponding to two molecular[18,30] and one atomic[18] form of chemisorption. When only the 3*d* orbitals of nickel were involved in the H_2–M_2 interaction, one state, corresponding to the adsorption of atomic hydrogen, was detected.[18]

The complete neglect of differential overlap (CNDO) showed that, irrespective of the structure of the crystallographic face, the extent of the participation of the 4*s* orbitals in bond formation is much greater than that of the 3*d* orbitals.[20]

Calculations of the change in the density of the surface *d* and *sp* states of transition metals (M = Ni, Pd, W) in an M_9 cluster with the (100) structure of an f.c.c. lattice during the chemisorption of atomic hydrogen, carried out by the X_α discrete variation method, made it possible to reach various conclusions about the mechanism of the interaction of a hydrogen atom with a metal surface.[19] As a hydrogen atom approaches an Ni_9 cluster, as a result of Coulombic interaction with the cluster, the energy of the 1*s* level of the hydrogen atom is lowered considerably, and approaches the energies of the 4*sp* levels of nickel. Thus the interaction of the 1*s* orbital of the hydrogen atom takes place primarily with the molecular orbital of the Ni_9 cluster situated at the bottom of the valence zone and including mainly the 4*s* and 4*p* orbitals of the nickel atom (Fig.1). This leads to the formation of two new levels: a bonding $1a_1$ and a hypothetical antibonding $2a_1'$; the latter interacts with the 3*d* orbitals of nickel, leading to the production, in the valence zone of the cluster, of a $2a_1$ level (with an energy ~4 eV lower than the Fermi level), characteristic of the H–M bond.[19] The formation of a new level situated 5.9 eV (Ni [31]) or ~5.6 eV (Fe [32]) below the Fermi level has been detected in an ultraviolet spectroscopic study of the adsorption of hydrogen.

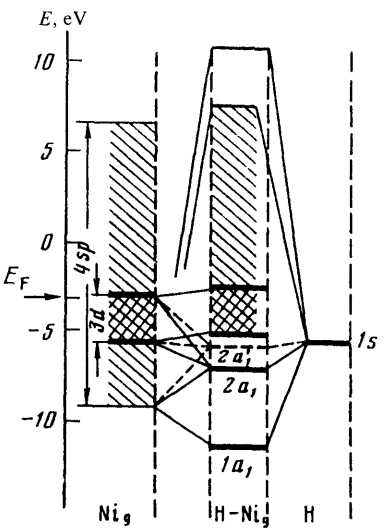

Figure 1. Schematic diagram of the interaction of the 1*s* orbital of a hydrogen atom with the 4*sp* and 3*d* orbitals of an Ni_9 cluster[19] (E_F is the Fermi level).

As a result of the formation, in the valence zone of the metal, of the antibonding $2a_1'$ level, produced as a result of the interaction of the 1*s*(H) and 4*s*(Ni) states[19] (see Fig.1), the population of the Ni–Ni bond becomes negative, leading to repulsion of neighbouring nickel atoms and to a decrease in the strength of the M–M bond in the lattice. It should be noted that in calculations of the adsorption of hydrogen on Pd and W [19] in the valence zone of the cluster H–M_9 only the

formation of the bonding level was observed; this is due to the differences in the electronic structures of Ni (the lowest occupied energy levels of the 3*d* zone are appreciably higher than the bottom of the 4*sp* zone) and Pd (the positions of the bottoms of the 4*d* and 5*sp* zones coincide). These data are in good agreement with the fact that nickel hydride, unlike palladium hydride, is unstable.[19]

The participation of both the *d* and *sp* surface states of transition metals in H–M bond formation was also detected experimentally in a study of the state of the surface of a solid during the adsorption of hydrogen.[33–36] The use of NMR [33] to study the adsorption of hydrogen on polycrystalline Cu, Pt, and W made it possible to reveal two adsorption states on the surface of Pt and W specimens, characterised by differences in the magnitude and direction of the resonance shift, and one adsorption state for Cu; the latter is a consequence of the participation of only the 4s orbitals of the metal in H–M bond formation.

Comparison of the directions of the resonance shifts in the adsorption of hydrogen on Pt and W with that obtained for Cu [33] shows that both the 5*d* and the 6*s* electrons take part in H–M bond formation. For Pt, the contribution of the 5*d* states to the production of both types of adsorption is much greater than that of the 6*s* states, whereas for W, predominant participation of the 5*d* orbitals is observed only for one less mobile (that is more firmly bound) adsorption state.

The predominant role of the 4*sp* states of the metal in H–M bond formation was detected in a study of the adsorption of hydrogen on the (111) face of a single crystal of nickel by photoelectron spectroscopy.[34] Comparison of the photoemission spectra obtained with gradual decrease in the degree of covering of a nickel surface with hydrogen (Fig.2) shows that the surface states of the metal are displaced to higher energies and gradually quenched in the range of energies corresponding to the 4*sp* zone of Ni (~0.25–0.50 eV below the Fermi level, see Fig.2). At the same time, the surface 3*d* states of nickel undergo practically no changes with increase in the time of exposure of the specimen in hydrogen.[34]

The predominant participation of the *sp* orbitals for Ni [34,36] and of the *d* orbitals for Pt and Pd [33] in H–M bond formation has been related to the differences in the electronic structures of these metals.[33,34]

According to quantum-chemical data, the H–M bond energy is determined by the extent of the participation of the surface *d* and *sp* states of the metal in the interaction with hydrogen, which in turn is determined by the structure of the chemisorption active centre.[15–17,20,22] Calculated data obtained by the extended Hückel method on the extent of the participation of the valence 3*d* and 4*s* electrons in the adsorption of atomic hydrogen on different crystal faces of nickel show that the role of the 4*s* orbitals of the metal increases with increase in the strength of the H–M bond, whereas the contribution of the 3*d* orbitals is greater for weak interactions with hydrogen; thus the population of the overlap of the 1*s* orbital of the hydrogen atom with the $3d_{z^2}$ and 4*s* orbitals of nickel changes as follows in the series of faces (110), (100), (111) (with decrease in the strength of the bond): 0.0452, 0.0526, and 0.0600 for the $3d_{z^2}$ orbital, and 0.1589, 0.1479, and 0.1399 for the 4*s* orbitals.[15]

The same regular features are observed for the chemisorption of molecular hydrogen.[21] For weak chemisorption of a hydrogen molecule (long H–Ni bond and short H–H bond) for the periodic model of the surface [an ideal crystal lattice, containing 250 atoms, with the f.c.c. structure, (100) face], the greatest contribution to bond formation is made by the 3*d* orbitals of nickel (Table 1), whereas with increase in the strength of the H–Ni bond, the participation of the 4*sp* states of the metal in adsorption predominates. For the cluster model of chemisorption, irrespective of the size of the particle, the 3*d* states of the metal make a smaller contribution to bond formation than the 4*sp* states (Table 1). The contribution of the *d* or *sp* orbitals of the metal to the interaction with hydrogen is determined by the structure of the chemisorption active centre.[15–17,22,25,37]

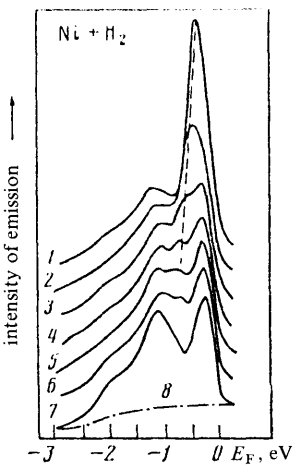

Figure 2. Photoelectron spectra of the (111) face of a single crystal of nickel for different degrees of covering of the surface by hydrogen:[34] *1*) original specimen; *2*) specimen kept in H_2 at 0.2 Langmuir; *3*) at 0.4; *4*) 0.6; *5*) 0.8; *6*) 1.0; *7*) 1.2; and *8*) (spectrum corresponding to complete saturation of the surface with hydrogen) 10.0 Langmuir (1 Langmuir = 10^6 mmHg). The broken line shows the displacement of the surface states with increase in the degree of covering of the surface.

Table 1. Contribution of the surface 3*d* and 4*sp* states of nickel to the formation of the H_2–M bond.[21]*

r (Ni–H), Å	r (H–H), Å	Ni–H bond population		r (Ni–H), Å	r (H–H), Å	Ni–H bond population	
		3*d*	4*sp*			3*d*	4*sp*
Periodic model of the surface				Ni_8 cluster			
2.0	0.74	0.410	−1.355	2.0	1.20	2.015	5.147
2.0	1.00	1.027	−0.010	Ni_{14} cluster			
2.0	1.20	3.096	2.830				
1.5	1.20	7.764	8.155	2.0	1.20	2.463	5.857

*The calculations were carried out by the extended Hückel method.

The EHM has been used to calculate the values of the energy of adsorption of atomic hydrogen and the population of the overlap of the 1*s* orbital of hydrogen with the 3*d* and 4*sp* orbitals of nickel for 11 different types of adsorption complex ("surface molecules").[16,17] Comparison of the energies of adsorption ΔE_{ads} obtained for the restricted periodic model of the surface and for the cluster model shows that on all crystallographic faces, the bond between the

hydrogen atom and one nickel atom (position *A*) is preferred (ΔE_{ads} has values from −2.80 eV to −2.46 eV) to the formation of multicentre bonds with the hydrogen atom situated between two (position *B*, ΔE_{ads} between −2.60 eV and −2.23 eV), three, or four (position *C*, ΔE_{ads} between −2.38 eV and −2.24 eV) nickel atoms. Irrespective of the number of bonds formed by the hydrogen atom with the metal atoms, the 4*sp* states of nickel play the greatest part in the interaction. The adsorption of hydrogen on all types of centre is accompanied by the formation of a negatively charged form of hydrogen;[15–17] the magnitude of the charge is determined by the structure of the active centre, and amounts to −0.35 e for centres of type *A*, −0.30 e for centres of type *B*, and −0.25 e for centres of type *C*.

Analogous data on the strength of the bond formed by a hydrogen atom adsorbed on a nickel surface in positions *A*, *B*, or *C* were obtained in Ref. 22, again by the EHM; the maximum displacement of charge from the metal to the hydrogen atom (−0.725, −0.605, and −0.536 e), the greatest population of the bond between the hydrogen atom and the nearest nickel atom (0.428, 0.317, and 0.237), and the maximum decrease in the total energy of the H–M system (−1118.445, −1118.080, and −1117.599 eV for adsorption on the centres *A*, *B*, and *C* respectively) correspond to the adsorption of the hydrogen atom on the centre of type *A*.

On the other hand, calculations of the stability of the multicentre bond of the chemisorbed hydrogen atom on nickel, carried out by the CNDO [20,38] and Wolfsberg–Helmholtz MO [6] methods for the adsorption of atomic hydrogen on the *A*, *B*, and *C* centres of the (100), (110), and (111) faces of a single crystal of nickel showed that an increase in the number of metal atoms taking part in bond formation with the hydrogen atom is accompanied by a significant increase in the bond energy: −1.6, 2.8, 3.2, and 3.0 eV for an H atom combined with one, two, three, and four nickel atoms.[38] Irrespective of the type of adsorption centre and crystallographic face, however (as in Refs. 15 and 17), negative charge is displaced from the metal to hydrogen (0.2 e); the magnitude of the charge changes little with change in the structure of the active centre.

Evidence of the preferential adsorption of hydrogen on centres formed by three, four, or five metal atoms (centres of type *C*) is also provided by the results of an experimental study of the chemisorption of hydrogen by low-energy electron diffraction,[39–46] energy-loss spectroscopy,[40] and inelastic neutron spectroscopy,[46,47] which showed that best agreement between the experimental and calculated data on the change in the structure and electronic state of the metals during the chemisorption of hydrogen is observed when multicentre models of chemisorption ($H–M_n$) are used.

2. Model of the Dissociative Chemisorption of Hydrogen

Quantum-chemical calculations of the energy of interaction in an $H_2–M_n$ system (where M = Ni, Pt, Pd) make it possible to reach various conclusions about the mechanism of the dissociative chemisorption of hydrogen and to determine the reasons for the production and to predict the relative height of the energy barrier to rupture of the H–H bond.[12,14,18,22,48]

The interaction of the molecular orbitals of hydrogen with the molecular orbitals of an Ni_{13} cluster (adsorption at the centre of the crystallographic (111) face of an icosahedron) leads to an appreciable change in the electronic structure of the metal (Fig. 3). At the bottom of the 3*d* zone, a new band ϕ^* (−9.571 eV) appears, formed mainly by the contribution of the antibonding $1s\sigma_u$ state of hydrogen and the valence level of the metal, including an appreciable proportion of the *d* state. The production, in the valence zone of the cluster, of a level containing antibonding states of hydrogen, and the appreciable transfer of electrons to this level from the *d* zone of the metal (−0.19 e) leads to a significant decrease in the strength of the H–H bond and is responsible for the dissociation of the hydrogen molecule.[22]

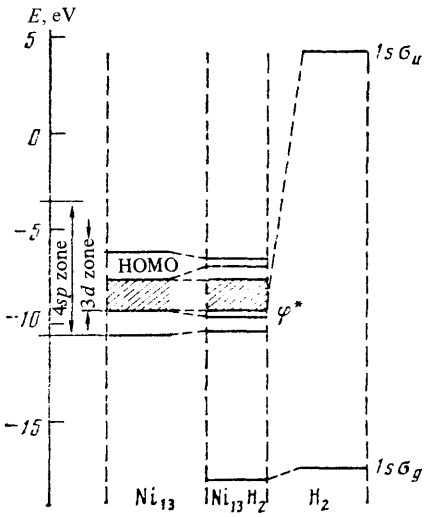

Figure 3. Schematic diagram of the interaction of the electron levels of the hydrogen molecule and an Ni_{13} cluster.[22]

A similar mechanism for the dissociation of molecular hydrogen in its adsorption on transition metals of the fourth period (Ti–Ni) was proposed[12] on the basis of MO LCAO calculations of the adsorption of a hydrogen molecule on a cluster formed by two metal atoms (M–M distance 2.5 Å). Since the hydrogen molecule does not have electron levels situated close to the 3*d* zone of the metal† (the magnitude of the 1*s*(H)–3*d*(Ni) overlap integral is ~0.1, whereas for 1*s*(H)–4*s*(Ni) it is ~0.5), the adsorption of molecular hydrogen takes place as a result of the donor–acceptor interaction of the occupied 1*s* orbital of hydrogen with the unoccupied bonding 4*s* orbitals of the metal.[12] The hydrogen molecule is positively charged.[12,27] The subsequent movement of the hydrogen molecule along the reaction coordinate (that is decrease in the H–M distance) is accompanied by the interaction of the antibonding 1*s* and 4*s* orbitals of the hydrogen molecule and the metal atom, leading to the formation of a new level in the valence zone of the $H_2–Ni_2$ cluster and the transfer of the 3*d* electrons of nickel to this level.[12]

The height of the energy barrier to the dissociation of molecular hydrogen is determined by the position of the 4*s* antibonding and 3*d* levels of the metal;[12] the higher these

†According to Ref. 22, the 3*d* zone of nickel in the Ni_{13} cluster lies in the energy range from −9.232 eV to −7.652 eV, and the *sp* zone in the range from −10.624 eV to −4.488 eV, whereas the bonding and antibonding levels of the hydrogen molecule have energies of −17.56 eV and 4.17 eV respectively.

levels on the energy scale, the more closely they approach the antibonding 1*s* levels of the hydrogen molecule, and hence the more readily the antibonding 1s(H) and 4s(M) states interact and the more readily the 3*d* electrons of the metal are transferred to the newly formed molecular orbital.

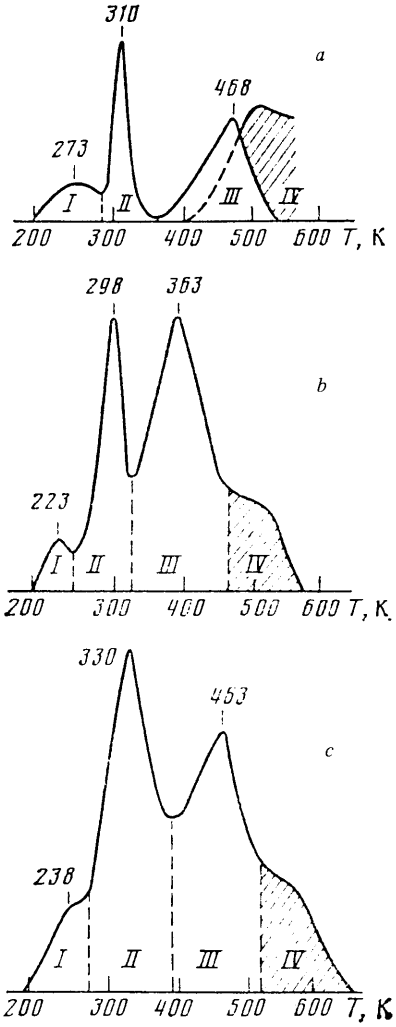

Figure 4. Spectra of the desorption of hydrogen from α-Fe (*a*), α-Co (*b*), and Ni (*c*) blacks (T_{ads} = 573 K);[50,52,54] *I,II,III*) forms of adsorbed hydrogen; *IV*) (hatched region) dissolved hydrogen.

Thus an analysis of theoretical and experimental studies of the mechanism of the chemisorption of hydrogen on transition metals of period IV shows that the adsorption of hydrogen takes place as a result of the interaction of the 1*s* states of the hydrogen molecule with the surface 4*sp* and 3*d* states of the metal atoms, with the preferential participation of the *sp* states. This interaction leads to the formation, in the valence zone of the metal, of a new level containing an appreciable proportion of the antibonding states of hydrogen and the 4*s* states of the metal, and to the transfer of the 3*d* electrons of the metal to this level, and hence to the dissociative chemisorption of hydrogen on the surface of the transition metals. The nature and strength of the H–M bond formed is determined by the extent of the participation of the 4*sp* and 3*d* states of the metal in the interaction; the greater the contribution of the *sp* states, the stronger the resulting H–M bond. The contribution of the *d* or *sp* states of the metals to the interaction in turn is determined by the electronic structure of the metal and the structure of the adsorbed complex.

The above data on the mechanism of the chemisorption of hydrogen on transition metals can be compared with the results of the study of the state of hydrogen in metal blacks of the iron sub-group (Fe, Co, Ni), obtained by temperature-programmed desorption.[49–54]# The reaction of hydrogen with these metals leads to the production of four forms of hydrogen, due to the existence of different types of adsorption complexes on the surface of the blacks studied (Fig.4). From the kinetics of the desorption, forms I and II were classified as molecular, and form III as an atomic form of chemisorption. The energetic uniformity of the most strongly bonded hydrogen of form IV, detected for Fe, Co, and Ni (the complete removal of the hydrogen of form IV under isothermal conditions at the temperature of the start of the desorption of the hydrogen of this form), together with published data on the solution of hydrogen in metals of the iron sub-group, made it possible to classify the hydrogen of form IV as hydrogen dissolved in the bulk of the metals studied;[50,53,54] the regular features of the solution of hydrogen will be examined in the next section.

A study of the distribution with respect to the activation energy of desorption of the hydrogen adsorbed in forms I, II, and III showed that part of the atomic hydrogen of form III (~40–50%) is characterised by similar values of the activation energy of desorption. The energetic uniformity of this fraction of the atomic hydrogen of form III on the surface of non-noble metals is due to the adsorption of hydrogen on centres of a single type (possibly one-centre adsorption), whereas the firmly bound and energetically less uniform fraction of the hydrogen of form III corresponds to the adsorption of hydrogen atoms on centres of different types (a multicentre bond of the form $H–M_n$, where n = 2, 3, 4, 5). Thus data on the state of hydrogen on the surface of non-noble metals (Fe, Co, Ni), obtained by thermal desorption, provide evidence of the greater strength of the multicentre $H–M_n$ bonds.

Comparison of the thermal desorption characteristics of hydrogen for the series Fe, Co, Ni (Table 2) shows that the strength of the bond produced by molecular forms of hydrogen tends to increase along the period; there is an increase in the temperature at which desorption is complete and in the proportion of molecular adsorption. The observed increase in the strength of the bond and increase in the proportion of molecular adsorption on going from Fe to Ni correlates with the change in the radius of the metal atoms along the period, leading to a downward displacement, on the energy scale, of the unoccupied bonding 4*s* levels of the metal, and to their maximum approach to the bonding 1*s* level of the hydrogen molecule. This last feature leads to a lowering of the energy barrier to the formation of the

#The Ni and Co black specimens studied were obtained by the reductive decomposition of the formates in a stream of H_2 at 573 K and 623 K. Fe black was prepared by decomposing iron nitrate and then reducing the oxides in H_2 at 773 K (30 h).

adsorbed complex H_2–M_n(Table 2).[12,18,26,27] The relative concentration and bond strength of the atomic adsorbed hydrogen on Fe, Co, and Ni blacks, on the other hand, decreases slightly from Fe to Ni (Fig.4 and Table 2). According to calculated data,[12,26,27] this may be due to an increase in the energy difference between the antibonding 1*s* level of hydrogen and the 4*s* antibonding and 3*d* levels of the metals involved in H–M bond formation, leading to an increase in the energy barrier to the dissociation of the hydrogen molecules (Table 2).

Table 2. Experimental[49–54] and calculated[26,27] characteristics of different forms of hydrogen on Fe, Co, and Ni.

M	*r*, Å	$T_{end\ des.}$, K	[H_2], %	$E(H_2\text{–}M)^*$, kJ mole^{-1}	$l_{H_2\text{–}M}$, Å	$E_{des.\ at.}$, kJ mole^{-1}	[H], %	E_{diss} (H_2–M), eV
Fe	1.26	343	39.1	−128.04	1.95	56.8	60.9	7.94
Co	1.25	313	44.4	−149.47	1.81	47.2	55.6	9.14
Ni	1.24	393	56.8	−172.35	1.75	45.2	43.2	10.95

Notes: *r* is the atomic radius; $T_{end\ des.}$ the temperature of the end of the desorption of molecular hydrogen; [H_2] the fraction of molecular hydrogen; $E(H_2\text{–}M)$ the energy of the complex H_2–M; *l* the equilibrium length of the H_2–M bond; $E_{des.\ at}$ the activation energy of the desorption of the atomic hydrogen of form III; [H] the fraction of atomic hydrogen; and $E_{diss}(H_2\text{–}M)$ the dissociation energy of the complex H_2–M.

*Calculated data.

Thus the experimental data on the variety of forms and the change in the quantity and bond strength of molecular and atomic hydrogen in the series Fe, Co, Ni [49–57] agree with the results of quantum-chemical calculations on the chemisorption of hydrogen, taking account of the electronic structure of both hydrogen and the metals.[12,13,15–22,27,30,58]

III. SOLUTION OF HYDROGEN IN METALS

1. Dependence of the Solubility of Hydrogen on the Electronic Structure of Transition Metals

The study of the solubility of hydrogen in the metals of the iron sub-group (Fe, Co, Ni) is of considerable practical importance. A number of monographs and reviews have been devoted to the problem of the solution of hydrogen in massive specimens (films, membranes, wires, etc.),[59–65] but published data on the solubility of hydrogen in dispersed metals are few and contradictory.[66–70] Since Fe, Co, and Ni are used as catalysts mainly in the dispersed state, it is of interest to determine the quantitative characteristics of the solubility of hydrogen in these metal blacks.

The main regular features of the solution of hydrogen in transition metals can be examined first. In recent years, increasing attention has been paid to the search for correlations between the ability of transition metals to dissolve hydrogen and their electronic structure.[67–72] Attempts are being made to establish the relationship between the solubility of hydrogen and the difference in the electron densities of the metal and hydrogen,[73] the concentration of valence electrons,[73,74] the density of states on the Fermi surface of the metal,[74,75] etc.

The main regular features of the change in the structure of the valence zone of the 3*d* and 4*d* transition metals with increase in the number of hydrogen atoms introduced into the lattice are qualitatively similar, as shown by calculations of the electronic structures of the hydrides of these metals with the stoichiometric composition, containing hydrogen as the proton.[71,76] On going from the pure metal to the compound containing 5 at.% hydrogen in the bulk of the metal ($MH_{0.05}$), a new metal–hydrogen level is produced, which lies below the conductivity zone and which is formed by the *s* states of hydrogen and hybridised *s*–*d* states of the metal;[71,76] further increase in the hydrogen concentration in the bulk of the metal is accompanied by broadening of the metal–hydrogen level.[71] Comparison of the electronic structures of pure palladium and the palladium–hydrogen system[75] indicates that the Fermi level is displaced to higher energies; the density of states on the Fermi surface decreases considerably.

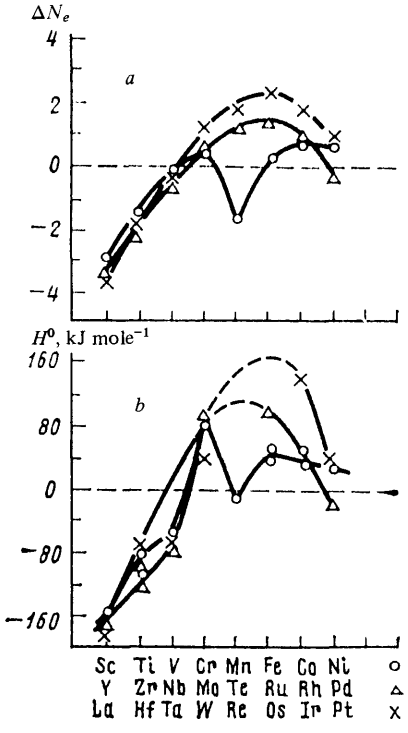

Figure 5. Change in the difference in the electron density ΔN_e on the metal and hydrogen atoms (*a*) and the heat of solution H^0 of hydrogen (*b*) along the 3*d*, 4*d*, and 5*d* periods[73] (the unit of density is ~6 × 10^{22} electron cm^{-1}).

Data obtained in calculations of the change in the electronic structure of transition metals during their saturation with hydrogen[71] have made it possible to estimate the heat of formation of the hydrides of 3*d* and 4*d* transition metals ΔE as the difference between the total energies of the zones of the

pure metal and compounds with different stoichiometric compositions. The stable hydrides of elements from the left-hand side of the fourth period (Sc, Ti, V) are formed with the liberation of considerable quantities of heat (from −40 kJ mole^{-1} to −200 kJ mole^{-1}). The formation of the products of the interaction of hydrogen with metals from the right-hand side of the period (Fe, Co, Ni, Cu; Fig.5*b*) is accompanied by the absorption of heat (from +40 kJ mole^{-1} to +90 kJ mole^{-1}).[71]

According to Ref.73, the transition metals which lie at the start of the 3*d* and 5*d* periods and which have a lower electron density than that on the hydrogen atom are also capable of dissolving hydrogen exothermally to give stable hydrides (Figs.5*a* and 5*b*). Metals with a higher electron density than that on the hydrogen atom dissolve only small quantities of hydrogen, with the absorption of heat (Figs.5*a* and 5*b*).[73]

According to Ref.74, depending on their position in the periodic system, the transition metals can be divided into two groups differing in the influence of dissolved hydrogen on the strength of the bonds formed by the atoms in the metal lattice: 1) metals whose *d* level is less than half filled; and 2) metals containing more than six valence electrons.

The introduction of the 1*s* electron of the hydrogen atom into the electron zone of metals of the first type increases the strength of the bond formed by the atoms in the lattice, leading to the formation of stable hydrides [60,71,73] (the metals of sub-groups III–V of the periodic system); the strength of the bond between the atoms in the lattice of metals of the second type (the transition metals of sub-groups VI–VIII) decreases when the 1*s* electron of the hydrogen atom is introduced (hydrogen brittleness). According to the Engel–Brewer theory,[77,78] this influence of dissolved hydrogen on the strength of the bond formed by the metal atoms in the crystal lattice is due to a change in the number of unpaired *d* electrons in the transition metals. The additional 1*s* electron of the hydrogen atom increases the number of unpaired electrons in metals whose valence zone is less than half filled, leading to an increase in the strength of the bond between the atoms in the lattice. For metals of the second type, whose outer level contains more than six electrons, the 1*s* electron of the hydrogen atom lowers the total number of unpaired electrons, leading to a decrease in the strength of the M–M bond in the crystal.

The dependence of the quantity of dissolved hydrogen on the number of unpaired *d* electrons in the outer level of the metal atom is clearly observed for transition metals with a small number of *d* electrons (d^2–d^4; Ti, Zr, V, La, Hf, etc.); the element with the smallest number of *d* electrons corresponds to the highest solubility of hydrogen and the greatest increase in the strength of the M–M bond.[74]

For metals with a valence level which is more than half filled (Fe, Co, Ni, Ru, Rh, Pd, etc.), best agreement between the calculated and experimental data on the extent of the solution of hydrogen is obtained using a model which relates the ability to dissolve hydrogen to the density of states on the Fermi surface of the given metal;[74] a higher density of states (Fig.6*a*) corresponds to a greater ability to dissolve hydrogen. These models have been used[74] to calculate the magnitude of the change in the strength of the M–M bond when the 1*s* electron of the hydrogen atom is introduced into the valence zone of the metal. The introduction of the additional electron increases the strength of the Ti lattice (ground state $3d^24s^2$) by 7.1%, whereas the bond between the atoms in the Ni lattice (ground state $3d^84s^2$) is weakened by 8.57%.

Comparison of calculated data on the extent of the disordering of metal lattices when hydrogen is absorbed[74] (Fig.6*b*) with the heats of solution of hydrogen[73] (Fig.5*b*) shows a distinct correlation between these quantities: the greater the decrease in the strength of the interaction between the metal atoms when the 1*s* electron of hydrogen is introduced (Fig.6*b*), the greater the endothermic effect of solution (Fig.5*b*).

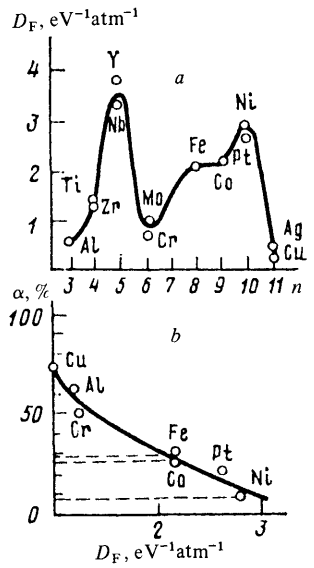

Figure 6. Density of states D_F on the Fermi surface (*a*) and extent of the disordering of the lattice α for 3*d* transition metals when hydrogen is dissolved in them (*b*) [74] (*n* is the number of electrons in the outer levels).

2. Influence of the State of the Surface on the Extent of the Penetration of Hydrogen into Metal Lattices

A significant unsatisfactory feature of theoretical methods for studying the solution of hydrogen by transition metals is the fact that no account is taken of the contribution of processes taking place on the metal surface during the solution of hydrogen. The absorption of hydrogen by the bulk of the metal is a complex multistage process, involving the adsorption and dissociation of the hydrogen molecule, the penetration of hydrogen atoms into the bulk, and diffusion in the volume of the metal.[59,61,63] Calculations[79] have shown that for metals characterised by an exothermic effect for the solution of hydrogen, the heat liberated during adsorption is sufficient for the penetration of the hydrogen atom into the bulk of the metal.

When hydrogen dissolves in metals for which this process is endothermic (Fe, Co, Ni), the heat liberated during the adsorption of hydrogen is insufficient for the penetration of the hydrogen atom into the bulk of the metal; penetration can take place only at high temperatures, when the adsorbed hydrogen atom acquires sufficient energy to overcome the energy barrier to penetration into the bulk of the metal.[79]

Analysis of the influence of various factors on the rates of the processes taking place on the surface of iron, nickel, and other transition metals during the solution of hydrogen in them[61] shows that change in the extent of the defect character (disperse nature) of the surface (plastic deformation,

the application of strokes, scratches, polishing, sintering at high temperatures[80-83]), its chemical composition (surface coatings[81,84,85]), or temperature[62,80,86-90] leads to a considerable change in the rate of penetration of H atoms into the bulk.

The rate of the penetration of hydrogen atoms into the bulk (ν) at high temperatures (>670 K) obeys the law $\nu \sim p^{1/2}$ (where p is the hydrogen pressure), indicating that solution is preceded by dissociation of the hydrogen molecule.[59,63,64] At temperatures <670 K, deviation from the $\nu \sim p^{1/2}$ relationship is observed, and the kinetic curves show inflections in the temperature range ~470–670 K [61,62,80,86-90] (Figs.7 and 8). According to Ref.61, the existence of the inflection is due to a change in the mechanism of solution; at temperatures <670 K (before the inflection), the surface reactions involving the dissociation of molecular (or the recombination of atomic) hydrogen take place at slow rates, that is they determine the rate of penetration; the activation energy of the penetration of hydrogen in this temperature range is high (107.0 kJ mole^{-1} for Fe). At temperatures >670 K (after the inflection), when the surface reactions take place readily and do not limit the rate of penetration of hydrogen, the activation energy of this process is only 37.6 kJ mole^{-1} (Fe) and practically coincides with the activation energy of diffusion.[87]

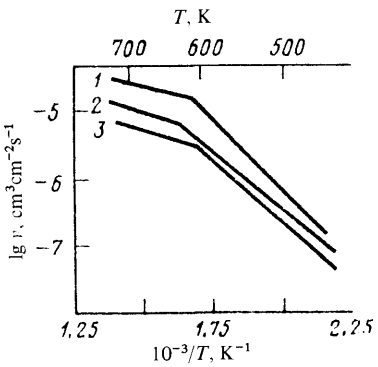

Figure 7. Temperature dependence of the rate of penetration of hydrogen V through iron membranes of different thickness l:[87] 1) l = 0.25 mm, 2) l = 0.5 mm, 3) l = 1.0 mm.

The role of the atomisation of molecular hydrogen in the process of solution in metals has been clearly demonstrated in a study of the permeability of a nickel membrane for deuterium previously ionised under gas-discharge conditions and for deuterium from the molecular state.[88] For the ionised deuterium, the temperature dependence of the rate of penetration (Fig.8) does not show an inflection (curve *1* in Fig.8), whereas for the non-ionised deuterium, at temperatures >630 K, as in Ref.87, a change in the rate of penetration of deuterium atoms into the bulk of the metals takes place (an inflection is observed; curve *2* in Fig.8). The activation energy of the penetration of deuterium is 61 kJ mole^{-1} at T < 630 K, and 10.5 kJ mole^{-1} at T > 630 K.[88]

The position of the point of inflection on the curve giving the temperature dependence of the rate of penetration of hydrogen depends markedly on the extent of the defect character (disperse nature) of the metal surface;[61,80-83,91] with change in the surface structure of the specimen, for example as a result of plastic deformation,[80] the inflection (~660 K) is displaced to higher temperatures (~790 K).

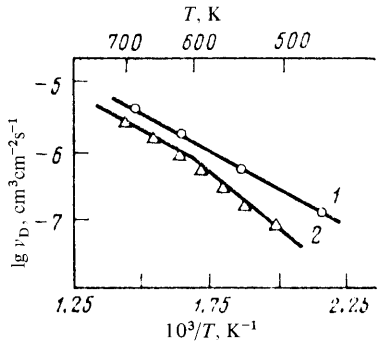

Figure 8. Temperature dependence of the rate of penetration of deuterium ν_D through a nickel membrane under gas-discharge conditions (*1*) and from the molecular phase (*2*).[88]

Change in the chemical composition of the surface layer of the specimen is also reflected in the rate of penetration of hydrogen into the bulk of the metal.[81,84,85] Covering an iron membrane with a thin layer of palladium[81] or other materials highly active in the atomisation of hydrogen (Ni and Pd blacks) leads to a marked increase in the rate of the penetration of hydrogen, whereas layers of Cu or Ag on an iron membrane surface decrease the magnitude of the hydrogen flux.[84] The application of thin coatings changes the electronic structure of metal surfaces, leading to an increase or a decrease in the rate of the dissociation or recombination of hydrogen;[61] for example, a gold membrane, which is practically impermeable to hydrogen, begins to allow it to pass freely if its inner surface is covered with a thin layer of nickel (thickness ~1 × 10^{-5} cm).[85]

Thus the dissolution of hydrogen in metals at temperatures <670 K is limited by surface reactions (adsorption, dissociation; recombination, desorption). The deviation of the values of the rate of penetration from the $\nu \sim p^{1/2}$ law at T < 670 K has been related[61] to a decrease in the number of active centres on the surface with decrease in the degree of dispersion of the metal, to the shielding action of surface impurities inactive with respect to the dissociation of hydrogen, and to the presence on the surface of chemisorbed hydrogen which does not have a sufficient reserve of energy for penetration into the metal lattice.[61]

The decrease in the rate of the stage involving the recombination of atomic hydrogen (or the dissociation of molecular hydrogen on the surface of nickel films, accompanied by an increase in the activation energy of the process at low temperatures, has been attributed[62,92] to the formation of a nickel hydride β-phase, whose catalytic activity in the recombination of atomic hydrogen is ~3 times lower than that of pure nickel.[92,93] Calculation of the standard free energy (G^0) of the H–M system for the reaction

$$4M + H_2 \rightarrow 2M_2H$$
$$M = Ni, Pd$$

has shown, however, that the formation of nickel hydrides at atmospheric pressure and relatively low temperatures is thermodynamically unlikely, since under these conditions the

value of G^0 for the NiH system is +23.6 kJ mole^{-1}, whereas for the formation of stable hydrides PdH, $G^0 = -11.8$ kJ mole^{-1}.

The preparation of stable hydrides of iron, cobalt, and nickel by the direct reaction of the metal with hydrogen is possible only under extremely severe conditions, at hydrogen pressures >10–20 thousand atm and temperatures >500 K.[62, 65,94] A study of the solubility of hydrogen in palladium and nickel, carried out using calculation methods,[95] showed that the formation of stoichiometric nickel hydrides (H/Ni = 1) is possible at hydrogen pressures not less than 28 thousand atm.

The study by various modern methods (X-ray diffraction, NMR, magnetic methods, etc.) of the state of hydrogen in the volume of metals which absorb it endothermally has indicated that the hydrogen atom transfers the 1*s* electron to the unfilled *d* zone of the metal, and is present in the lattice as a proton.[59,60,63,79,97] According to calculations,[96] the effective charge of the hydrogen atom is +0.45 e in the Pd lattice, +0.53 e for Ni, and +0.26 e for Fe.

There are at present two widely encountered views on the equilibrium position of a hydrogen atom introduced into a metal lattice. The authors of Refs.63 and 98, who used the precision method of secondary X-ray spectra to study the state of iron saturated with hydrogen, concluded that the hydrogen endothermally absorbed by the metal is present as a proton, inserted into the electron cloud of the metal atoms ("proton gas"). On the other hand, the theoretical calculation of the equilibrium positions of hydrogen atoms in metals which crystallise with a face-centred cubic lattice shows that in a structure of this type, the particles introduced occupy octahedral vacancies.[99,100] Experimental neutron diffraction studies of the structure of the products of the reaction of palladium and nickel with hydrogen also indicate that the protons occupy octahedral positions in the f.c.c. lattice.[101,102]

Calculation of the positions of hydrogen atoms introduced into the body-centred cubic lattice of α-Fe, Ta, V, and Nb [103] showed that in α-Fe the hydrogen atoms occupy only octahedral positions, in Ta and Nb the hydrogen can occupy octahedral and tetrahedral positions, and in V it occupies only tetrahedral lattice positions.

It is of considerable interest to identify the surface active centres by means of which the hydrogen atoms penetrate into the metal lattice. Kinetic and thermodynamic calculations[104,105] have shown that for metals which dissolve hydrogen exothermally (for example Pd), the heat of the adsorption of hydrogen on the centres responsible for its solution should not exceed ~68 kJ g-atom^{-1}, so that more firmly bound forms of chemisorption cannot be in equilibrium with absorbed hydrogen.[104] Experimental confirmation of the suggestion that hydrogen penetrates into the bulk of palladium via centres which chemisorb hydrogen with a relatively low bond energy is provided by data obtained by thermal desorption.[79, 106,107] The first portions of hydrogen are adsorbed on a Pd wire (104–306 K) on centres with a high M–H bond energy (heat of adsorption 60–120 kJ g-atom^{-1}); solution of hydrogen does not take place. Dissolved hydrogen appears in the desorption spectrum only when hydrogen covers the regions of the surface with a low heat of chemisorption (30–60 kJ g-atom^{-1}) (this is the low-temperature range of hydrogen desorption, characterised by a high energetic uniformity).

The authors of Ref.106, who used a micro-gravimetric method to study the kinetics of the sorption and desorption of hydrogen, concluded that the penetration of hydrogen into the palladium lattice takes place via regions which adsorb weakly bound forms of hydrogen (heat of adsorption 7 kJ g-atom^{-1}). Calculation of the thermal effects of all stages of the sorption of hydrogen showed that the movement of hydrogen from the state preceding the penetration of hydrogen into the bulk of palladium is energetically more favourable (activation energy of absorption 15 kJ g-atom^{-1}) than its migration along the surface to centres with a high heat of adsorption (activation energy of migration 55 kJ g-atom^{-1}).[106]

The conclusion that the desorption of absorbed hydrogen takes place via adsorption centres with a low hydrogen–metal bond energy was also previously reached for dispersed Pd,[107] Ta, and W.[108]

The solution of hydrogen in dispersed Fe, Co, and Ni was studied by temperature-programmed desorption[49,50,53,54] to determine the temperatures of the start of the solution and the removal of dissolved hydrogen from the bulk of metals; to differentiate adsorbed and dissolved forms of hydrogen according to the temperature ranges and activation energies of desorption; to estimate quantitatively their concentrations in the metals; and to study the influence of the surface adsorbed forms on the removal of hydrogen from the lattices of these metals.

Dissolved hydrogen appears in α-Fe black at $473 < T \lesssim 573$ K, in α-Co black at 373–423 K, and in Ni black at 298 to 373 K, that is on going from one metal to another along this triad, the temperature of the start of the solution (curve *3* in Fig.9) and the activation barrier to this process decrease; E_{abs} for α-Co black is 18 kJ mole^{-1},[52] whereas for Ni black this energy is 2.5 kJ mole^{-1}.[50] In accordance with the model relating the solubility of hydrogen in transition metals to their electronic structure,[74] the minimum heats of the endothermic solution are observed for metals which have the maximum density of states on the Fermi surface. For nickel, which has the highest density of states on the Fermi surface (curve *1* in Fig.9) and the lowest heat of solution (curve *2* in Fig.9), the absorption of hydrogen requires the minimum expenditure of energy compared with Fe and Co (curve *3* in Fig.9).

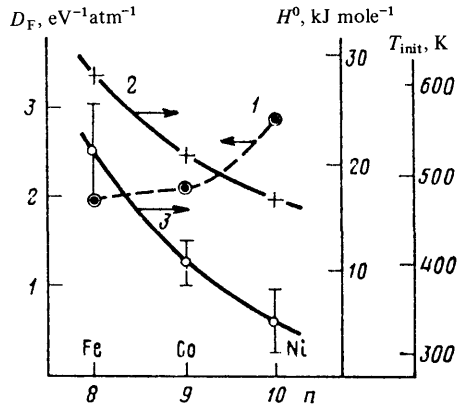

Figure 9. Correlation between the heat of solution H^0 (*2*),[73] the temperature of the start of the solution of hydrogen T_{init} (*3*),[53,54] and the density of states on the Fermi surface D_F (*1*)[74] for the metals of the first triad of Group VIII of the periodic system (n is the number of outer electrons).

Comparison of the solubility of hydrogen in α-Fe, α-Co, and Ni blacks shows that the absorption capacity of α-Fe black with respect to hydrogen is 10^3 times greater than that

for α-Co and Ni blacks; the ratio of the number of hydrogen atoms absorbed by the metal to the total number of metal atoms in the specimen is ~1 for α-Fe black, 1.7×10^{-3} for α-Co black, and 1.4×10^{-3} for Ni black. The sharp decrease in the quantity of dissolved hydrogen in the order Fe > Co > Ni is evidently also due to differences in the electronic structures of the metals. The solubility of hydrogen is higher, and the solution takes place with an exothermic effect, in those transition metals on whose atoms the electron density is lower than that on hydrogen atoms.[73] In metals which dissolve hydrogen with an endothermic effect, the electron density on the metal atoms is generally higher than that on hydrogen atoms.[73] For iron, however, the difference in the electron density on the Fe and hydrogen atoms is much lower than that for Co and Ni (see Fig.6a), and this is apparently responsible for the higher solubility of hydrogen in iron. The high absorption capacity of α-Fe with respect to hydrogen (specimen saturation temperature 773 K) is quantitatively comparable with that of Pd [1,2,8,107,109,110] (saturation temperature ~298 K), in good agreement with the similarity in the values of the electron density on the α-Fe and Pd atoms.[73]

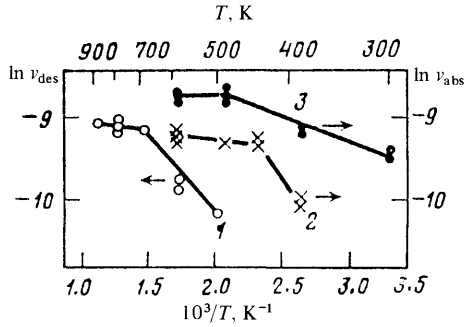

Figure 10. Temperature dependence of the rate of desorption of dissolved hydrogen from α-Fe black (*1*) and the rate of adsorption of hydrogen by α-Co (*2*) and Ni (*3*) blacks.[52,54]

In the determination of the activation energy of the desorption or absorption of dissolved hydrogen, the curves giving the temperature dependence of the rate of desorption (α-Fe black, Fig.10) [53,54] or absorption of hydrogen (α-Co and Ni blacks, Fig.10, see Ref.111 for the method of calculation) showed inflections at temperatures of 673 K for α-Fe, 423 K for α-Co, and 473 K for Ni. At low temperatures (before the inflection), the activation energy for the desorption of hydrogen from α-Fe black is 14.6 kJ $mole^{-1}$; E_{abs} for hydrogen for α-Co and Ni blacks is 18.0 kJ $mole^{-1}$ and 2.5 kJ $mole^{-1}$ respectively. At high temperatures (after the inflection), the slope of the straight lines decreases, and the values of E_{des} and E_{abs} indicate that the processes take place with practically no activation barrier; E_{des} for α-Fe black is 2.5 kJ $mole^{-1}$, and E_{abs} has the values ~0.4 kJ $mole^{-1}$ and <0.1 kJ $mole^{-1}$ for α-Co and Ni blacks respectively. Comparison of the temperatures of the liberation of adsorbed (Fig.4) and dissolved (Fig.4 and curve *3* in Fig.9) forms of hydrogen from α-Fe, α-Co, and Ni blacks indicates that the absorption or desorption of dissolved hydrogen with low activation energies takes place at a temperature above that corresponding to the complete removal of adsorbed forms of hydrogen from the surface.[49-54]

Data on the temperature boundaries of the liberation of adsorbed and dissolved forms of hydrogen and the start of the desorption and solution of hydrogen in the bulk of Fe, Co, and Ni blacks, which dissolve hydrogen endothermally (Figs.4 and 9), indicate that, in contrast to metals which dissolve hydrogen exothermally (Pd, Ta, W),[105-108] the removal of hydrogen dissolved in Fe, Co, and Ni takes place on the sections of the surface which chemisorb firmly bound forms of hydrogen.

Thus the systematic study of the processes involved in the chemisorption of hydrogen for metal blacks of the iron subgroup has revealed the regular features of the change in the strength of the bonds formed by atomic and molecular hydrogen, and also the absorption power of the blacks, and has made it possible to relate these characteristics to the positions of the metals in the periodic system. The data obtained on the concentration, forms, and bond energies (E_{des}) of hydrogen, which is one of the components of catalytic processes, can be used to develop active catalytic systems and to determine their mechanism of action.

Moreover, the quantitative characteristics obtained for the desorption of dissolved hydrogen from dispersed Fe, Co, and Ni may be useful in the development of processes preventing the corrosion breakdown of these metals.

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Complexes of Molecular Oxygen with Organic Molecules

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Molecular oxygen forms complexes with organic molecules. Evidence for such complex formation and its manifestations are described and criteria are formulated whereby one can distinguish the usual equilibrium complexes from impact (collision) complexes. The principal types of complexes and the electron orbitals with the aid of which the species combined in the complex come into contact are examined.
The bibliography includes 30 references.

CONTENTS

I. Introduction 117
II. Electronic spectroscopy and NMR of the oxygen complexes 117
III. Oxygen complexes of organic and organoelemental molecules 120
IV. Oxygen complexes of organofluorine molecules 125
V. Oxygen complexes in chemical reactions 126

I. INTRODUCTION

Molecular oxygen is a participant in an enormous number of physical and chemical processes. The question whether it reacts as a free molecule or whether its reactions are preceded by some kind of interaction, physical or "semichemical", with the other reactants or with other molecules is important for the chemistry of oxidation processes (where the involvement of oxygen in the initiation of thermal and photochemical oxidation is important), for the photonics of molecules (where oxygen participates in the quenching of electronically excited states, energy transfer, and sensitisation), and for the optical properties and the chemistry of the atmosphere (photochemical reactions of oxygen, the change in the transparency of the atmosphere as a result of the optical absorption by the possible oxygen complexes, etc.)

This review discusses the following question: in what state is molecular oxygen present in organic liquids and does it interact with organic molecules and how does such interaction take place—via the formation of "normal", equilibrium complexes or in contact pairs where the overlap of the electron shells of the reacting species takes place only at the instant of contact between them on collision (this state of the pair is sometimes referred to as an impact or collision complex). The spectroscopic manifestations (in electronic and magnetic resonance spectroscopy), which permit conclusions concerning the nature of the oxygen complexes and about the electron orbitals involved in complex formation, are examined: the chemical manifestations and chemical consequences of the complex formation reactions of oxygen and of its solvation by organic molecules are discussed.

II. ELECTRONIC SPECTROSCOPY AND NMR OF THE OXYGEN COMPLEXES

The manifestations of the formation of complexes between molecular oxygen and organic molecules were first observed by electronic spectroscopy. Evans[1,2] was the first to observe a marked increase of the intensity of the bands corresponding to the forbidden S_0-T_1 transition in the absorption spectra of aromatic hydrocarbons under the influence of dissolved oxygen. It was shown that the vibrational structures of these bands and of the phosphorescence spectra of the hydrocarbons are identical: even the positions of the 0–0 transitions coincide. Both these findings demonstrate reliably that oxygen induces the removal of the spin prohibition of the electronic transitions in many aromatic molecules:[3] it is also clear that the removal of the spin prohibition requires contact between the molecules and the merging of the electron clouds of the molecules of O_2 and the other reactant.

Another manifestation of the complex formation is the appearance of a new structureless absorption band at $\lambda \geq 300$ nm, which is attributed to the complex of O_2 with an aromatic molecule and is believed to be a charge-transfer band. For benzene, $\varepsilon_{max} \cong 900$ at the maximum of this band, while $\varepsilon_{max} \cong 0.4$ for the S_0-T_1 band.[3] Such bands have also been observed for many other compounds—alcohols, ethers, and saturated hydrocarbons. A band at 340 nm has been observed for the O_2 + naphthalene system and has been interpreted as one corresponding to the simultaneous electronic transition of the O_2 molecule to an excited singlet state and of the naphthalene molecule to a triplet state with retention of the overall spin and energy.[3] All these features indicate the occurrence of an interaction of the O_2–organic molecule pair which entails the merging of the electron clouds of the reacting species. The state of the pair in which this interaction takes place is short-lived and the interaction itself is apparently weak.

The nature of the complexes remains obscure. It has been suggested that the species combined in the complex are linked by van der Waals forces, but this conflicts with the spectroscopic characteristics of the complex formation. It is also not confirmed by measurements of the nuclear paramagnetic relaxation of ethylene and ethane in the gas phase in the presence of O_2:[4] the marked difference between the polarisabilities of these molecules is in no way manifested in the nuclear relaxation, which rules out any serious contribution by the van der Waals interaction.

Razuvaev and co-workers used the phenomenon of the quenching of the luminescence of excited molecules by oxygen to investigate the interaction of the latter with organoelemental compounds.[5–8]. It is known that oxygen quenches excited states in both gaseous and liquid phases with a high efficiency and this fact also indicates the occurrence of an interaction between the electron clouds of the oxygen and

excited molecules†. It is most probable that the complexes formed under these conditions are of the donor–acceptor type in which the reacting species are combined via specific orbitals with formation of "semichemical" bonds between them. A partial charge transfer between the species apparently takes place in such a complex but the question whether this state is a collision complex or a normal, equilibrium complex cannot be resolved unambiguously solely from electronic spectroscopic evidence.

Razuvaev and co-workers measured the luminescence intensity of solutions of organoelemental molecules in hexane frozen at 77 K and compared such intensities with solutions containing oxygen and deoxygenated solutions. In the presence of oxygen the intensity of the luminescence of the molecules falls markedly. If it is assumed that the O_2 complexes do exist and that they do not luminesce, it is easy to derive a relation between the luminescence intensity in the presence of oxygen (I) and in its absence (I_0) and the concentration (or pressure) of oxygen:

$$I_0/I = 1 + K[O_2]; \; I_0/I = 1 + K\gamma p_{O_2} \quad , \qquad (1)$$

where γ is the Henry constant for the solubility of oxygen (the authors adopted $\gamma = 1.5 \times 10^{-2}$ mol litre^{-1} atm^{-1} for hexane) and K is the complex formation equilibrium constant for the organic molecule M:

$$M + O_2 \overset{K}{\rightleftarrows} M \cdot O_2 \quad .$$

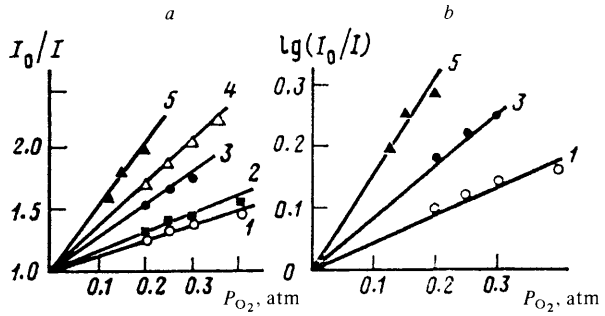


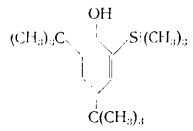
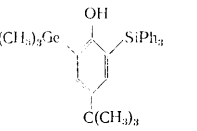
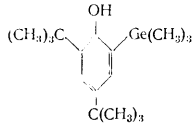
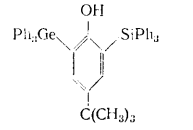
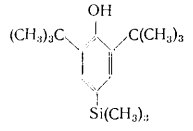
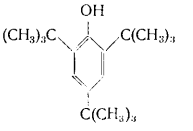
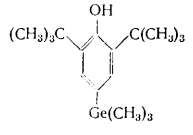
Figure 1. Dependence of the intensity of the fluorescence of organoelemental molecules on the oxygen pressure in terms of the variables of Eqns.(1) (*a*) and (2) (*b*): 1) Ph_4Si; 2) Ph_4Ge; 3) Ph_4Sn; 4) Ph_3SiH; 5) Ph_4Pb.[6]

†In order to avoid the quenching effect of oxygen in liquid solutions, prolonged evacuation of the latter (up to several days) is required. This fact is frequently accounted for by the existence of stable long-lived oxygen complexes. As will be shown below, this view is in all probability erroneous; the long duration of the quenching effect of oxygen is apparently associated with the presence of other quenching agents—comparatively stable intermediate oxidation products, which gradually decompose in the absence of oxygen (on evacuation). These products are sometimes stable and it is then altogether impossible to eliminate fully the quenching effect by evacuation.

Eqns.(1) resemble in their form the familiar Stern–Volmer equation and are indeed valid (Fig.1). The equilibrium constants K have been obtained from them. For the compounds Ph_3E (E = P, As, Sb, or Bi), Ph_4E (E = C, Si, Ge, Pb, or Sn), Ph_3SiH, Ph_3GeH, $(CH_3)_4Sn$, etc., the measured constants K are in the range 90–400 litre mol^{-1}; they are higher for Ph_3N (650 litre mol^{-1}) and for the compound $PhGeH_3$, we have K = 2000 litre mol^{-1}.[6] For organomercury compounds of the type Ph_2Hg, $(C_6F_5)_2Hg$, PhHgCl, $PhHgCCl_3$, etc., the constants K are in the range 250–500 litre mol^{-1};[6] the constants for organoelemental phenols are listed in Table 1.

The experimental technique used to measure the complex formation constants on the basis of the quenching of the luminescence is simple and convenient, but one must be sure that the equilibrium $M + O_2 \rightleftharpoons M.O_2$ is attained at 77 K. On freezing, the diffusion of oxygen is greatly retarded (particularly in a solid solution) and at 77 K there is therefore a possibility that the equilibrium corresponding to a higher temperature becomes "frozen". In other words, at 77 K the $M + O_2$ system may not be at equilibrium. Furthermore, the method presupposes a homogeneous distribution of both oxygen and the luminescing molecules in the solid solution, which necessitates certain precautions when this method is employed.

Table 1. The equilibrium constant for the oxygen complexes of phenols (77 K).[6]

Phenol	K, litre mol^{-1}	Phenol	K, litre mol^{-1}
	300		270
	350		280
	280		380
	300	—	—

Another feature of the luminescence method for the measurement of the equilibrium constant is that one must rule out the possibility of the static quenching of the luminescence of the molecules by oxygen via the Perren mechanism. The static quenching presupposes that there is a sphere with a radius r around the O_2 molecule within which the luminescence of the molecules is quenched, while outside it no quenching takes place. This quenching mechanism is referred to as the inductive-resonance mechanism; it gives rise to the following relation between the luminescence intensity and the

oxygen concentration c:

$$I_0/I = \exp(\alpha c), \quad (2)$$

where $c = \gamma p_{O_2}$ (mol litre^{-1}) and $\alpha = {}^4/_3\pi r^3 N_A$ (litre mol^{-1}) the overall volume of the quenching spheres (here r is expressed in dm and N_A is the Avogadro number). In terms of the variables of Eqn.(2), the dependence of $\lg(I_0/I)$ on c should be represented by a straight line, from the slope of which it is possible to determine the radius of the quenching sphere r. Fig.1*b* illustrates such relations for certain data taken from Fig.1*a*. Evidently Eqn.(2) sometimes holds just as satisfactorily as Eqn.(1) and in order to distinguish them it is necessary to make measurements over a wider range of concentrations of the quenching agent (oxygen). Only then is it possible to establish whether the decrease in the luminescence intensity is caused by complex formation or by the static oxygen quenching.

It has been shown[9] that oxygen in the presence of benzene does not influence the intensity of the luminescence of organoelemental compounds, i.e. O_2 does not behave as a quenching agent under these conditions. This is an important fact, which implies, firstly, that benzene molecules also form complexes with O_2, competing with the molecules of the organoelemental compounds for oxygen, and, secondly, that the oxygen attached to the benzene molecule is incapable of combining with the molecules of the organoelemental compounds and of quenching their luminescence. These results also demonstrate that the luminescence quenching method used[5-9] to analyse the complex formation by molecular oxygen is apparently not complicated by static quenching processes and that the quenching itself is of the exchange-resonance type, determined by the contact between the electron clouds of the reacting species (as in the analogous processes involving quenching by oxygen in gases and liquids).

Thus electronic spectroscopy reveals a number of features indicating a definite interaction of oxygen with organic molecules: the change in the intensity of the electronic transitions, the removal of spin prohibitions, the appearance of new bands in the electronic absorption spectrum, and the quenching of excited states by oxygen. There exist also arguments in support of the view that this interaction cannot be reduced solely to the universal van der Waals interaction and that it has a specific donor–acceptor character. However, electronic spectroscopy cannot yield more definite information about the nature and dynamics of this interaction; more unambiguous results are provided by NMR spectroscopy.

The oxygen molecule has two π-electron systems in two perpendicular planes passing through its D_{∞},h axis. Each of the π-electron systems incorporates three electrons, two of which form an unshared pair, while the third is a single, unpaired electron.[10] The O_2 molecule has a triplet ground state, i.e. the spins of the two single electrons are added together to give an overall spin $S = 1$. The energy of the magnetic dipole interaction of the single electrons is 33000 G and the spin–lattice relaxation time of the electrons is very short, amounting to approximately 50 μs at 1.5 K and $\lesssim 10^{-12}$ s at 300 K.

If the oxygen in the liquid is not in the free state and is partly linked to other molecules, forming complexes with the latter (so far it is immaterial whether these are the usual or collision complexes), then such interaction is inevitably accompanied by the merging of the electron clouds of the reacting species and the partial transfer of the unpaired electrons of the oxygen to the other species—the ligand. The appearance of an unpaired electron in the organic molecule (in both the usual and collision complexes) creates a local magnetic field at the nuclei and induces a line shift in the NMR spectrum of this molecule (it is referred to as the paramagnetic shift). The local magnetic field of the unpaired electron at the ligand nucleus periodically appears and vanishes because the complex is periodically formed and decomposes; each time the orientation of the unpaired electron and hence the direction of the local magnetic field which it generates at the ligand nucleus is random. This leads to the partial averaging of the local magnetic field. Furthermore, such averaging occurs also in the complex itself if the electron relaxation (the reorientation of the electron spin) is rapid. For oxygen complexes, the averaging of the local field of the electron at the ligand nucleus takes place via both mechanisms—via both the formation and decomposition of the complexes and as a result of the short electron relaxation time ($\lesssim 10^{-12}$ s). As a result of the averaging process, the paramagnetic shift of the NMR signal of the ligand in the complex is given by[11]

$$\Delta_0 = \delta_L - \delta_0 = -a\left(\frac{\gamma_e}{\gamma_n}\right)\frac{\gamma_e S(S+1)H_0}{3kT} = -a\alpha, \quad (3)$$

where δ_0 is the position of the NMR peak of the free molecule [in parts per million (p.p.m.)], δ_L is the position of the same peak in the spectrum of the complex, i.e. when the molecule becomes a ligand, γ_e and γ_n are the gyromagnetic ratios for the electron and the nucleus, H_0 is the external magnetic field strength, S the spin of the paramagnetic species (for oxygen, $S = 1$), and a the electron–nucleus (hyperfine) interaction (HFI) constant characterising the local magnetic field of the electron at the ligand nucleus. The parameter α is defined by Eqn.(3), is temperature dependent, and can be readily calculated; in particular $\alpha = 200$ p.p.m. G^{-1} for protons at 26 °C, for the ^{19}F nuclei at the same temperature, we have $\alpha = 211$ p.p.m. G^{-1}, while at 40 °C $\alpha = 202$ p.p.m. G^{-1}.

The paramagnetic peak shifts in the NMR spectra of organic molecules in the presence of oxygen are an unambiguous and reliable manifestation of complex formation by oxygen—a manifestation of the combination of the electron clouds of the oxygen and organic molecules. The magnitude and direction of the paramagnetic shift depend on the sign of the HFI constant involving the ligand nucleus in the complex. The sign of the HFI constant demonstrates the mechanism whereby the unpaired electron is transferred in the complex from oxygen to the ligand and in which orbitals it is located, while the magnitude of the constant determines the density of the unpaired electron transferred from oxygen to the s shell of the ligand atoms. It is linked to the spin density $\rho(0)$ in the s shell of the atom by the familiar Fermi relation:

$$a = ({}^8/_3)\pi\gamma_e\gamma_n\rho(0). \quad (4)$$

The NMR method makes it possible to solve also another important problem—namely that of the complexes (of the usual or collision types) in which the paramagnetic shifts arise. If the usual complexes are formed and the complex formation equilibrium

$$M + O_2 \overset{K}{\rightleftarrows} M \cdot O_2 \quad (I)$$

is established, as a result of which the organic molecule M is periodically either in a free state, or in the complex $M.O_2$ then the paramagnetic shift Δ of the NMR peak observed experimentally is defined by the equation[11]

$$\Delta = \delta - \delta_0 = \Delta_0 p_L, \quad (5)$$

where p_L is the mole fraction of the complex $M.O_2$. Here δ_0 is, as before, the position of the NMR peak in the spectrum of the free molecule and δ is its position in the presence of

oxygen:

$$\delta = \delta_0 p_0 + \delta_L p_L \ . \qquad (6)$$

Condition (6) describes the averaging of the position of the NMR peak due to the rapid exchange of the molecule between the two states (the free molecule and the ligand in the complex with oxygen), whose mole fractions are p_0 and p_L respectively. Eqn.(5) is obtained taking into account Eqn.(6) and the self-evident normalisation condition $p_0 + p_L = 1$.

After determining p_L on the basis of equilibrium (I), i.e.

$$p_L = \frac{K[O_2]_0}{1 + K[M]_0} \qquad (7)$$

and substituting it in Eqn.(5), we obtain

$$\Delta = \frac{\Delta_0 K[O_2]_0}{1 + K[M]_0} \ , \qquad (8)$$

where $[O_2]_0$ and $[M]_0$ are the concentrations in solution of oxygen and of the other molecules involved in the complex formation. The magnitude of this shift, referred to the concentration $[O_2]_0 = 1$ M (the reduced paramagnetic shift), will be designated by Δ^*:

$$\Delta^* = \frac{\Delta_0 K}{1 + K[M]_0} \ . \qquad (9)$$

Eqns.(8) and (9) can be expressed in a linear form:

$$\frac{[O_2]}{\Delta} = \frac{1}{\Delta_0}(K^{-1} + [M]) \ , \qquad (10)$$

$$\frac{1}{\Delta^*} = \frac{1}{\Delta}(K^{-1} + [M]) \ , \qquad (11)$$

where the subscripts to $[O_2]_0$ and $[M]_0$ have been omitted.

If the paramagnetic shifts arise in collision complexes which exist only when the two species are in contact during the period of their "settled" life, then the mole fraction p_L of such complexes can be easily calculated, provided that one knows the coordination number of the complex n (i.e. the number of nearest neighbours) and the probability that the test molecule M enters the first (contact) coordination sphere of the oxygen molecule:

$$p_L = \frac{[M \cdot O_2]}{[M]} = \frac{n[O_2][M]}{[M] + [N]} \cdot \frac{1}{[M]} = \frac{n[O_2]}{[M] + [N]} \ , \qquad (12)$$

where [N] is the concentration of other molecules in the mixture.

Evidently the concentration dependences of p_L and of the paramagnetic shifts for complexes of these two types differ appreciably. In order to distinguish such complexes, it is sufficient to investigate the concentration dependence of the paramagnetic shift and to test whether Eqns.(10) and (11) or (12) hold.

Finally the third advantage of NMR in the study of the oxygen complexes is the possibility of the direct measurement of the concentration of dissolved oxygen. For this purpose, the paramagnetic shifts are measured in solutions at different concentrations placed in two sealed tubes arranged coaxially one inside the other, the inner tube containing oxygen (under a pressure of 0.1–5 MPa depending on the oxygen concentration which it is desired to ensure in the solution). The concentration of the dissolved oxygen in the inner tube is determined from the distance between the NMR peaks in the spectrum of an inert solvent present in the inner and outer bulbs. The shift δ_χ of the peaks due to the inner tube relative to those of the outer tube is due to the magnetic volume susceptibility of the dissolved oxygen and is related to its concentration $[O_2]$ by the expression[12]

$$\delta\chi = (2\pi/3) \cdot 10^{-3} \chi_m [O_2] \qquad (13)$$

where χ_m is the molar magnetic susceptibility of oxygen:

$$\chi_m = \frac{4N_A\beta^2 S(S+1)}{3kT} = \frac{0.496 S(S+1)}{T} \ . \qquad (14)$$

Here N_A is the Avogadro number, β the Bohr magneton, and S the electron spin of the oxygen molecule; in particular at 26 °C we have

$$\delta_\chi \text{ (p.p.m.)} = 6.94\,[O_2], \qquad (15)$$

where the O_2 concentration is expressed on a molar scale.

Having measured the concentration dependence of the paramagnetic shifts (i.e. their dependence on the mixture composition) and the oxygen concentration, it is possible to test the validity of Eqns.(10)–(12) and to determine the type of complexes formed by oxygen and their quantitative characteristics (the equilibrium constants K and the HFI constants a).

III. OXYGEN COMPLEXES OF ORGANIC AND ORGANOELEMENTAL MOLECULES

The paramagnetic shifts of the NMR peaks induced by molecular oxygen have been observed in many investigations[11, 13–15] for a large number of various organic molecules. They were first observed by Polak and Navon,[13] but, owing to their low magnitude (the authors worked at low pressures up to 0.3–0.4 MPa), it was impossible to reach definite conclusions about the origin of these shifts. The concentration dependences of the paramagnetic shifts at high oxygen pressures were investigated only quite recently and reliable evidence has been obtained for the existence of the oxygen complexes.[11]

Buchachenko and Pokrovskaya[11] were interested primarily in the interaction of aromatic molecules, particularly benzene, with molecular oxygen. Their initial idea was that the interaction of oxygen with benzene would induce paramagnetic shifts of the benzene NMR peaks, which could be reckoned relative to the position of the NMR peaks of cyclohexane—the solvent which is traditionally regarded as inert and which the authors assumed would not interact with oxygen, i.e. its NMR peak would not undergo paramagnetic shifts.

An example of the recording of the NMR spectrum of a benzene–cyclohexane mixture (for the volume ratio $C_6H_6 : C_6H_{12} = 14 : 1$) is illustrated in Fig.2. The narrow peaks are due to benzene and cyclohexane in the bulb without oxygen and the broadened peaks are due to benzene and cyclohexane in the bulb containing oxygen. The oxygen-induced shift of the benzene peak is 172.9 Hz and the shift of the cyclohexane peak is 160.9 Hz. The difference between the shifts is 12.0 Hz and exceeds by two orders of magnitude the error of the measurement. Consequently, apart from the shifts caused by the magnetic susceptibility of the dissolved oxygen (which should be the same for benzene and cyclohexane), there exists also the paramagnetic shift $\Delta = 12.0$ Hz, which, as suggested in the beginning, is caused by the interaction of benzene with oxygen.

However, it is impossible to claim *a priori* which mixture component (benzene or cyclohexane) is inert in relation to oxygen. The paramagnetic shifts of the NMR peaks were therefore determined in the spectra of mixtures of benzene and cyclohexane of different composition and were analysed by two methods: it was initially assumed that cyclohexane is inert and the paramagnetic shifts of the benzene peaks

were reckoned relative to the cyclohexane peak (for example, the shift of 12.0 Hz for the $C_6H_6 : C_6H_{12} = 14 : 1$ mixture is due to benzene in this version). In the second method it was assumed that the paramagnetic shift is undergone by the cyclohexane peak and benzene is the inert solvent and that the ^1H NMR peaks of benzene do not undergo a paramagnetic shift; in this method the shift $\Delta = 12.0$ Hz for the above mixture was attributed to cyclohexane. The paramagnetic shifts Δ were converted into the reduced shifts Δ^*; the oxygen concentrations necessary for this recalculation were determined from total shifts of the NMR peaks of benzene.

The reduced shifts Δ^* are plotted in Fig.3 as a function of mixture composition; its analysis permits the conclusion which component (benzene or cyclohexane) is the one with which oxygen interacts. If it is assumed that the cyclohexane is inert in relation to oxygen, then the shifts of the benzene peaks reckoned relative to the cyclohexane peaks (curve 2) increase with increasing benzene concentration. This relation has no physical significance, since at a constant oxygen concentration the mole fraction of the benzene–oxygen complexes should diminish with increasing benzene concentration because the complexes are diluted by the free benzene molecules. As a result, the paramagnetic shift of the benzene peaks should diminish with the increasing benzene concentration; this prediction is completely in conflict with experiment.[11]

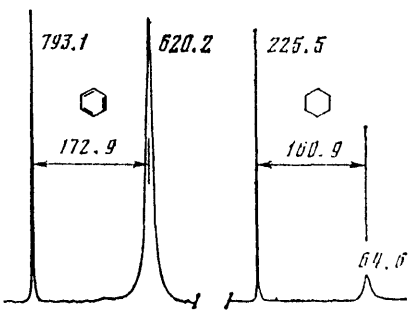


Figure 2. NMR spectrum of the benzene–cyclohexene mixture measured at a frequency of 100 MHz. The numerals opposite the NMR peaks indicate their frequencies (in herz) relative to hexamethyldisiloxane.[11]

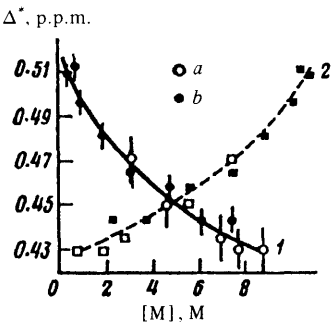


Figure 3. Concentration dependence of the reduced paramagnetic shifts Δ^*: 1) the shifts of cyclohexane peaks relative to benzene lines; 2) the shifts of benzene peaks relative to cyclohexane lines; temperature (°C): *a*) 20; *b*) 10.[11]

On the other hand, if it is assumed that the benzene molecules are inert with respect to oxygen, then the concentration dependence of the shifts of the cyclohexane peaks reckoned relative to the positions of the benzene peaks has the correct form: the mole fraction of the cyclohexane complexes and hence the shifts of the cyclohexane peaks diminish with increasing cyclohexane concentration. (Fig.3, curve 1). Furthermore, the concentration dependence of the paramagnetic shifts of the cyclohexane peaks obeys Eqn.(11) (Fig.4); the equilibrium constant for the complex formation reaction between cyclohexane and oxygen, calculated by Eqn.(11), is 1.6×10^{-2} litre mol^{-1}, while the HFI constant for the complex, averaged over all the ligand (cyclohexane molecules) protons is positive (the peaks shift in a weak field) and amounts to +0.15 G. If it is assumed that the transfer of the unpaired electron from oxygen in the complex takes place to only one of the twelve ligand hydrogen atoms (the bond between oxygen and the ligand is formed via this atom), then the HFI constant for this atom amounts to $0.15 \times 12 = 1.8$ G, which corresponds to the unpaired electron density in the 1s orbital of the hydrogen atom (approximately 0.36×10^{-2}). We may note that this density is positive, i.e. the unpaired electrons are transferred from oxygen to the ligand hydrogen atom via a delocalisation mechanism.

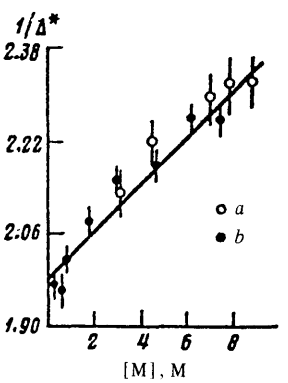


Figure 4. Dependence of the reciprocal of the reduced paramagnetic shift of the NMR peak of cyclohexane on its concentration in terms of the variables of Eqn.(11); temperature (°C): *a*) 20; *b*) 10.[16]

Thus it follows unambiguously and reliably from the analysis of the concentration dependence of the paramagnetic shifts that the cyclohexane NMR peaks shift to a greater extent under the influence of oxygen than do the benzene peaks. Since the paramagnetic shifts of the cyclohexane peaks are small, those for benzene are smaller still and in principle can be neglected and one can assume that the benzene peak does not undergo a paramagnetic shift at all. In terms of this approximation, benzene can be regarded as an inert solvent in the sense that its peak in the ^1H NMR spectrum hardly shifts and can be used as the reference signal for the measurement of the paramagnetic shifts of the peaks of all other molecules. Furthermore, it follows from this that the shift of the benzene peak is caused almost wholly by the magnetic volume susceptibility of the dissolved oxygen (Buchachenko and Pokrovskaya[11] gave direct experimental evidence for this fact) and can be used to measure its concentration.

Another important result consists in the fact that the interaction of oxygen with cyclohexane (and, as will be shown below, also with other molecules) takes place in the usual complexes and not in collision complexes, which is indicated by the validity of Eqns.(10) and (11) for the concentration dependence of the paramagnetic shifts. The same dependences hold for the paramagnetic shifts of the NMR peaks of the protons of *p*-difluorobenzene in benzene. The complex formation equilibrium constant is 0.25 litre mol^{-1} and the HFI constant for the protons is −0.01 G.

The absence (or more precisely the negligible magnitude) of the paramagnetic shifts of the proton NMR peaks for benzene does not strictly speaking imply that benzene is inert in relation to oxygen and is not involved in complex formation reactions with the latter. The absence of a shift can be a consequence of the fact that benzene forms with oxygen complexes of different types (for example via the C−H bond and the π-electron system) and the paramagnetic shifts of the proton signals induced in these complexes have different signs so that on average they fairly effectively cancel out. In order to test this hypothesis, the paramagnetic shift of the ^{13}C NMR peak of benzene was measured. In the benzene spectrum at 24 °C the shift $\Delta(^{13}C)$ was 0.49 p.p.m. at an O_2 concentration (determined from the shift of the proton resonance peak) of 0.123 M. Hence it follows that the reduced paramagnetic shift $\Delta(^{13}C) \cong 4$ p.p.m., i.e. its value is large, exceeding by an order of magnitude the paramagnetic shifts of the signals of the protons in cyclohexane. The presence of such a shift is direct evidence for the formation of a complex between benzene and oxygen. The shift is directed downfield, which implies that in the complex the positive spin density of the unpaired electron is transferred from oxygen to the π-electron system of the benzene molecule and the mechanism of this transfer involves direct delocalisation.

The most complete and reliable results have been obtained by Karmilov and co-workers,[14,15] but the paramagnetic shifts were measured in these investigations relative to the position of the NMR peak of cyclohexane, which was assumed to be inert with respect to oxygen. Bearing in mind the results of Buchachenko and Pokrovskaya[11] and introducing corrections for the paramagnetic shift of the cyclohexane peaks, it is now possible to find the true paramagnetic shifts for these molecules relative to benzene; the negative shifts correspond to an upfield displacement of the NMR lines, while the positive shifts correspond to a downfield displacement (Table 2). The difference between the signs and magnitudes of the paramagnetic shifts is striking. This fact constitutes the strongest evidence that the paramagnetic shifts are induced in the usual complexes of the molecules with oxygen and not in collision complexes, where the paramagnetic shifts are induced by the van der Waals interaction and should have the same sign for all the nuclei regardless of the chemical species to which they belong.

It is seen from the data in Table 2 that the signs and magnitudes of the paramagnetic shifts depend on the chemical structure of the ligand and obey definite rules. The NMR peaks of the protons in the OH and NH groups (in water, alcohols, and aniline, and pyrrolidine) as well as the CH groups in chloroform and CH_2Cl_2 undergo an upfield paramagnetic shift, i.e. in the complexes with oxygen the negative spin density of the unpaired electron appears on these protons. The signals of the protons of the aliphatic CH_2 and CH_3 groups (in alcohols, cyclohexane, hexamethylbenzene, dimethylaniline, *o*- and *p*-xylenes, tetramethyl-*p*-phenylenediamine, and cyclohexene) undergo downfield paramagnetic shifts, i.e. the positive spin density of the unpaired electron is transferred to these protons in the complex with oxygen.

Finally, the signals of the protons of aromatic rings (in toluene, *o*- and *p*-xylenes, *p*-difluorobenzene, naphthalene, and tetramethyl-*p*-phenylenediamine) undergo upfield paramagnetic shifts, which indicates the appearance of a negative spin density on these protons in the oxygen complex.

Table 2. The paramagnetic shifts Δ* of the NMR peaks of the molecules induced by the formation of their complexes with oxygen.

Molecule (ligand)	Group	Δ*, p.p.m.	Molecule (ligand)	Group	Δ*, p.p.m.
Water (in acetone)	OH	−0.52	*o*-Xylene	CH_3	+0.33
Methanol	OH	−0.32		⩾CH	−0.03
"	CH_3	+0.33	*p*-Xylene	CH_3	+0.34
Ethanol	OH	−0.52		⩾CH	−0.18
"	CH_2	+0.49	*p*-Difluorobenzene	⩾CH	−0.14
"	CH_3	+0.33	$(CH_3)_2N-C_6H_4-N(CH_3)_2$	CH_3	+0.35
Chloroform	CH	−0.42	"	⩾CH	−0.20
CH_2Cl_2	CH_2	−0.32	Cyclohexene	α-CH_2	+0.55
Phenylacetylene	≡CH	−0.52	"	β-CH_2	+0.40
$PhNH_2$	NH_2	−0.62	"	⩾CH	+0.10
Pyrrolidine	NH	−0.17	Cyclo-octadiene	CH_2	+0.37
Acetone	CH_3	+0.05		⩾CH	+0.20
$(CH_3)_3SiOSi(CH_3)_3$	CH_3	+0.02	Cyclo-octatetraene	⩾CH	+0.07
Cyclohexane	CH_3	+0.42	Naphthalene	α-CH	−0.43
Hexamethylbenzene	CH_3	+0.18	"	β-CH	−0.10
$PhN(CH_3)_2$	CH_3	+0.23			

These findings permit definite conclusions about the structure of the oxygen complexes and the nature of the orbitals involved in the "joining together" of the species in the complex. Molecules containing the OH and NH groups as well as those of $CHCl_3$ and CH_2Cl_2 add to the unshared electron pair of oxygen via their O−H, N−H, or C−H bonds (Fig.5*a*). These are complexes of the *n*−σ type (or hydrogen bonded complexes), in which oxygen provides the *n* orbital and the ligand the σ orbitals of the O−H, N−H, or C−H bonds. The negative spin density on the hydrogen atom of the bond involved in complex formation (O−H, N−H, or C−H) appears in this complex as a result of the spin polarisation of the hydrogen bond by the unpaired π electron of the oxygen molecule. The structure and the electronic interactions of these oxygen complexes resemble those of the anlogous complexes with participation of organic radicals.[16,17]

The aliphatic CH_2 and CH_3 groups add via the C−H σ-bonds to the π orbital of oxygen, forming π−σ complexes (Fig.5*b*); as a result of delocalisation, a positive spin density appears on the hydrogen atom of the ligand (as in the radical complexes of the same type[17]) and there is a downfield paramagnetic shift (in cyclohexane, the methyl groups of alcohols, amines, xylenes, toluene, etc.).[16]

Aromatic molecules apparently add via the π-electron system to the π orbital of oxygen, forming a π−π complex (Fig.5c); the unpaired π electron is then partly transferred to the π-electron system of the ligand from oxygen and induces, via the spin polarisation of the C−H bonds, a negative spin density in the 1*s* orbitals of the hydrogen atoms of the aromatic ring. The negative paramagnetic shifts for the aromatic protons in substituted benzenes and in naphthalene can be explained in precisely this way. This is also supported by the positive paramagnetic shift (downfield) of the signals of the ^{13}C nuclei of benzene (see above), indicating the appearance of a positive π-electron spin in the π-electron system of benzene.

However, we may note that the paramagnetic shifts of the peaks due to aromatic protons are small in absolute magnitude and those for benzene are altogether negligible, which implies that benzene (and apparently other aromatic molecules) form

complexes of two types: $\pi-\pi$, in which a negative spin density appears on the protons, and $\pi-\sigma$ (as for cyclohexane), in which a positive spin density appears on the protons via direct delocalisation. The almost complete and mutual cancellation of these two contributions for benzene ensures that the overall paramagnetic shift of the benzene protons is zero. In other paramagnetic molecules this cancellation is incomplete with the contribution by the $\pi-\pi$ complex predominating and an upfield paramagnetic shift.

The mutual cancellation of the paramagnetic shifts due to various complexes apparently takes place also for the acetone and hexamethyldisiloxane protons, for which the paramagnetic shifts are very small. In this case the positive shift due to the $\pi-\sigma$ complexes is compensated by the negative shift due to other complexes (for example, $n-\sigma$).

Special mention should be made of the paramagnetic shift of the signals due to the protons of double bonds (cyclohexene, cyclohexadiene, and cyclo-octatetraene). These shifts are directed downfield, are small in absolute magnitude, and depend on the chemical structure of the ligand. In these instances, too, two contributions are added together: the positive contribution due to the $\pi-\sigma$ complexes (via the direct delocalisation of the spin from the π orbital of oxygen to the C–H σ-bond (Fig.5*b*) and the negative contribution due to the $\pi-\pi$ complexes (delocalisation of the π-electron density from oxygen to the π-electron system of the double bond with subsequent spin polarisation of the C–H bonds attached to the double bond). The same mutual cancellation takes place in this instance as for aromatic protons; the only difference is that the $\pi-\sigma$ interaction makes the dominant contribution. The involvement of the double bonds in $\pi-\pi$ interaction and the presence of the positive spin density of the unpaired π-electron in the π-electron system of the double bonds are indicated by the considerable positive shift of the protons in the α-CH_2 group in cyclohexene, which exceeds that due to the protons of the β-CH_2 group. This additional positive shift of the signal of the α-CH_2 protons arises owing to the direct delocalisation of the unpaired π electron from the double bond to the α-CH_2 group via the hyperconjugation mechanism.

The π-electron spin density is also transferred from oxygen to the π-electron system of phenylacetylene (Table 2) as a result of $\pi-\pi$ interaction. It then induces, via spin polarisation, a negative spin density on the acetylene proton, which is accompanied by an upfield paramagnetic shift of the peak due to the latter.

The concentration dependence of the paramagnetic shifts has been investigated in mixtures of benzene with cyclohexane, *p*-xylene, cyclo-octadiene, hexamethyldisiloxane, *p*-difluorobenzene, and acetone. In most cases the dependence proved to be very weak and difficult to measure; this implies that the complexes with oxygen are weak and their stability constants at 20 °C are small and satisfied the condition $K[M] \ll 1$, i.e. $K \lesssim 10^{-2}$ litre mol^{-1}; for these complexes, $\Delta^* = \Delta_0 K$ (Table 2). The concentration dependence of the paramagnetic shift could be measured and the equilibrium constant and the constant for the hyperfine interaction in the complex could be determined only for cyclohexane and *p*-difluorobenzene.[11,16]

The paramagnetic shifts of the nuclei belonging to different fragments of the same molecule are different (Table 2). Thus in toluene the shifts for the aromatic and methyl protons are different not only in magnitude but also in sign. The same is characteristic of methanol, ethanol, xylene, and naphthalene, which implies that different structural elements of the same molecule interact with oxygen in different ways. Furthermore, the temperature dependences of the shifts for different groups of the same molecule are likewise different. Thus the shifts for the methanol methyl protons depend only slightly on temperature, while for the hydroxyl proton the temperature coefficient of the shift is 0.5 kcal mol^{-1}; in toluene the shifts for aromatic protons are almost independent of temperature, while for the methyl protons their dependence is pronounced with a temperature coefficient of 1.7 kcal mol^{-1}.[15]

The different temperature dependences of the shifts for different functional groups in the same molecule imply that the molecules interact with oxygen via individual fragments and not as a single whole, i.e. the interaction has a specific localised character. Furthermore, both these facts, namely

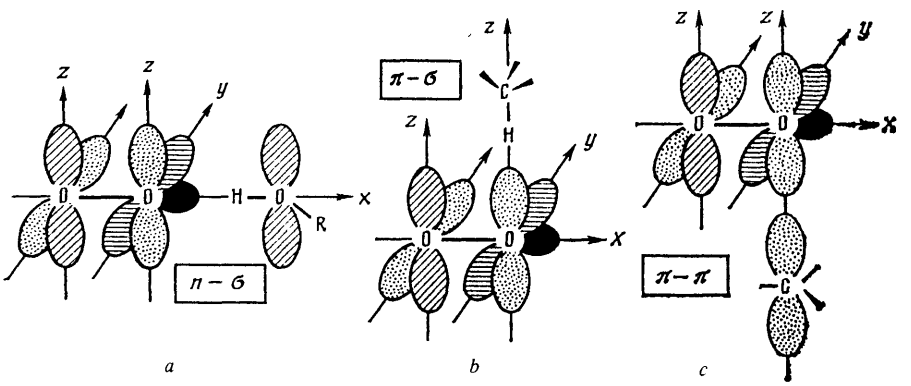


Figure 5. Molecular models of the oxygen complexes: *a*) the $n-\sigma$ complex in which oxygen provides the *n* orbital and the ligand the σ orbital of the O–H, N–H, or C–H bond; *b*) the $\pi-\sigma$ complex in which oxygen provides the π orbital and the ligand the σ orbital of the bond; c) the $\pi-\pi$ complex in which both oxygen and the ligand provide the π orbitals for the complex formation reaction.[16]

the different shifts and their different temperature dependences, demonstrate convincingly that the dominant type of interaction in the oxygen–organic molecule pair is equilibrium complex formation. As already stated previously, the paramagnetic shifts induced in collision complexes should be the same both in magnitude and in sign for all nuclei and in addition should be independent of temperature.

An important criterion used in the "recognition" of the complexes and the identification of the orbitals involved in complex formation is the competition between two or more ligands for the oxygen orbitals. This criterion was formulated in the analysis of the structures of radical complexes.[18] The idea is that the concentration dependences of the paramagnetic shifts of the solvated molecules depend on whether two different ligands add to the same oxygen orbital or to different orbitals. In the former case the ligands compete for their "site" in the given oxygen orbital, while in the latter they do not compete and add independently and autonomously to different orbitals. Clearly in the case of non-competing ligands the addition of one ligand should not influence the paramagnetic shifts of the signal due to the other ligand. On the other hand, such an influence should occur for the competing ligands, tending to "sit" on the same electronic orbital of oxygen. Thus it follows from the concentration dependence of the cyclohexane shifts in the presence of acetone, water, and tetramethylsilane that cyclohexane is a stronger ligand than water.[14] The molecules of methanol (hydroxy-group) and CCl_4 are not competing ligands, i.e. they add to different oxygen orbitals: the OH group of methanol adds to the *n* orbital and CCl_4 adds to the π orbital. Dimethylaniline (the CH_3 group) and CCl_4 are competing ligands, both molecules adding via their C–H and C–Cl bonds to the oxygen π orbital.[14]

The experimental results for the paramagnetic shifts of competing ligands are as yet insufficient to reach final conclusions about the detailed structure of the oxygen complexes. However, one can already reach the general preliminary conclusion that the oxygen π orbital is more active in complex formation than the *n* orbital. This property differentiates the oxygen complexes from those of organic radicals: in the latter case the *n* orbitals give rise to more stable complexes with organic molecules than the π orbitals.[17] This feature is apparently associated with the electronic structure of the oxygen molecule, in which the *n* orbitals in the π-electron system have not been formed distinctly and are strongly coupled with the π orbitals of single electrons, while the *n* orbitals of the 2*s* electrons are too "weak" for complex formation.

We may note that, for a number of molecules (acetone, chloroform, and phenylacetylene), considerable paramagnetic shifts of the NMR peaks due to the ^{13}C nuclei have also been observed;[14] this indicates a fairly pronounced overlap of the electron clouds of the interacting species in the oxygen complex and a far-reaching delocalis at ion of the spin density from the oxygen to the ligand. Thus for acetone (^{13}C in the CO group) the paramagnetic shift Δ^* at acetone concentrations of 1.5–4.5 M in benzene amounted to 0.2–0.5 p.p.m.[16] The ^{13}C peaks shifted downfield, indicating that a partly unpaired π electron is transferred to the π-electron system of acetone from oxygen. This transfer apparently proceeds via the π–π interaction (as in the complex with benzene).

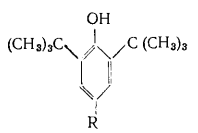
The paramagnetic shifts of the NMR peaks of the protons in diphenyl- and dibenzyl-mercury in the presence of oxygen have been measured[19] relative to cyclohexane. After introducing a correction for the cyclohexane shift, we obtain the true paramagnetic shifts for these organomercury molecules (Table 3).

Since both toluene and xylene form complexes with oxygen, it is evident that the phenyl and benzyl groups in the organomercury molecules should also add to oxygen. However, the marked difference between the paramagnetic shifts of these two groups of molecules (Table 3) shows that the complex formation with the mercury atom is the dominant process and makes the maximum contribution to the paramagnetic shifts for the organomercury molecules. The temperature dependence of the shift has also been measured for dibenzylmercury; the temperature coefficient is approximately 1 kcal mol^{-1}.[19]

Table 3. The paramagnetic shifts Δ^* (in p.p.m.) for the protons (CCl_4, 25 °C).[19]

Molecule	⩾CH	CH_3 (or CH_2)	Molecule	⩾CH	CH_3 (or CH_2)
Ph_2Hg	−0.47	—	Toluene	−0.07	+0.38
$(PhCH_2)_2Hg$	−0.22	−0.12	*o*-Xylene	−0.03	+0.33

The paramagnetic shifts for the protons of a number of phenols (including organoelemental phenols) of the type



have been measured;[20,21] their values, corrected for the paramagnetic shift of cyclohexane, are listed in Table 4.

Table 4. The paramagnetic shifts Δ^* (in p.p.m.) for the protons of phenols (CCl_4, 25 °C).

R	OH	Ring *meta*-protons	R	OH	Ring *meta*-protons
$C(CH_3)_3$	−0.20	+0.13	$Si(CH_3)_3$	−0.38	+0.05
CH_3	−0.12	+0.20	$Ge(CH_3)_3$	−0.64	+0.07
H	−0.14	+0.26	$SiPh_3$	−0.67	—
Cl	−0.25	+0.10	$GePh_3$	−0.97	—
NO_2	−0.57	−0.32			

A common property of the oxygen complexes of these phenols is an upfield paramagnetic shift of the peaks of the hydroxyl protons; this implies that the negative spin density of the unpaired electron appears on the hydroxyl proton in the complex. Evidently oxygen adds to the hydroxy-group of phenol via the unshared electron pair (hydrogen-bonded complex). Furthermore, the positive π-electron density is transferred to the π-electron system of the benzene ring in the complex and is distributed in the π-electron system of the ring in the same way as in aromatic alternant radicals: it is positive in the *o*- and *p*-positions and negative in the *m*-position. A positive spin density should then appear on the *m*-protons as a result of spin polarisation and their NMR signal should undergo a downfield paramagnetic shift (in agreement with experiment, see Table 4).

Another piece of evidence for the appearance of the unpaired π electron in the benzene ring of the ligand is the downfield paramagnetic shift of the signal due to the methyl group in the *p*-position in the spectrum of a phenol with

R = CH_3 (Δ^* = +0.61 p.p.m.); it arises as a result of the delocalisation of the π electron from the *p*-position of the benzene ring via the hyperconjugation mechanism.[20]

It is not clear whether the unpaired electron is transferred from oxygen to the hydroxy-group and to the π-electron system of the benzene ring in the same complex or different complexes (i.e. to the hydroxy-group in complexes of one type and to the π-electron system in those of another). It is incontrovertible that the paramagnetic shifts of the peaks in the spectra of element-containing phenols exhibit anomalies (Table 4), which implies that, apart from the interaction of oxygen with the hydroxy-group and the benzene ring, there is also a direct and significant (in magnitude) interaction of oxygen with the atoms of the elements. This conclusion is likewise valid for other organoelemental phenols investigated by Razuvaev et al.[21]

IV. OXYGEN COMPLEXES OF ORGANOFLUORINE MOLECULES

It is known that organofluorine hydrocarbons and their derivatives dissolve molecular oxygen effectively and are therefore used to transport the latter in blood substitutes and in liquid-phase respiration.[22,23] The state of oxygen in these solutions and the causes of its anomalously high solubility are unknown. The hypothesis has been put forward that organofluorine liquids have a "porous" structure with a large free volume which is accessible to oxygen, but it lacks any kind of foundation.

It is most likely that oxygen in organofluorine liquids exists in a state where it is partly bound in complexes. In order to test this hypothesis, a study was made of the paramagnetic shifts of the ^{19}F NMR peaks in the spectra of organofluorine molecules in the presence of dissolved oxygen.[24] Very large paramagnetic shifts were observed and their concentration dependence was found to obey Eqn.(11) (Fig.6), whence the complex formation equilibrium constants and the HFI constants for the ^{19}F nuclei were obtained (Table 5). Compared with the paramagnetic shifts of the ^{19}F NMR peaks, the proton resonance shifts of the molecules of compounds 2, 3, and 4 (Table 5) are negligible, i.e. the CH_2 and CH_3 groups and the double bonds are hardly involved in complex formation with oxygen, which implies that the interaction of oxygen with the molecules is localised exclusively at the fluorine atoms. The positive spin density is then transferred to the electronic orbitals of the fluorine atom (there is a downfield shift of the ^{19}F lines and the constant *a* is positive). The positive sign of the constant *a* implies that an interaction of the π–*n* type takes place in the complex, i.e. the π orbital of oxygen adds to the unshared electron pair of the fluorine atom. Approximately 0.1% of the unpaired electron is then transferred to the inner 2*s* shell of the fluorine atom.

Table 5. The equilibrium constants *K* and the HFI constants *a* for the complexes of O_2 with organofluorine molecules (40 °C).

No.	Molecule	*K*, litre mol^{-1}	*a*, G
1	C_6F_6	0.13±0.01	+0.49
2	$(CF_3)_3CCH{=}CH_2$	0.12±0.01	+0.36
3	$(CF_3)_2CCH{=}CHCH_3$	0.11±0.01	+0.28
4	$CF_3CF_2CF_2COO(CH_2)_3CH_3$	0.12±0.02	+0.37

It follows from the concentration dependence of the shifts that the transfer of the unpaired electron from oxygen to the organofluorine ligand and the paramagnetic shifts of the ^{19}F NMR peaks take place in equilibrium complexes and not in collision complexes; single-ligand complexes with a 1:1 stoichiometry of the interacting species, i.e. complexes of the type $M.O_2$, predominate under these conditions.

The equilibrium constants *K* for different molecules are fairly large and differ little from one another; in particular, they are almost identical (Fig.6) for the CF_3 and CF_2 groups of the molecules of compound 4 (Table 5). This constancy also indicates the localisation of the interaction of oxygen via the fluorine atom, in which the structure of the remainder of the molecule does not play an especially important role. Thus organofluorine molecules do indeed form fairly stable complexes with molecular oxygen in which the electron clouds of the interacting species overlap and there is a partial transfer of the unpaired electrons from oxygen to the ligand (the organofluorine molecule).

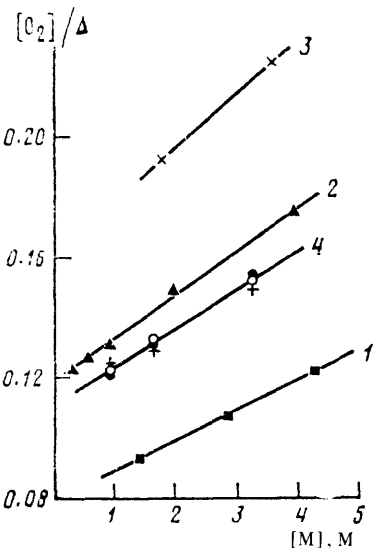


Figure 6. Concentration dependence of the paramagnetic shifts of the ^{19}F NMR peaks in terms of the variables of Eqn.(11); the numbers of the straight lines correspond to those of the compounds in Table 5.[24]

$K = 2.4 \times 10^{-2}$ litre mol^{-1} has been found reliably for *p*-difluorobenzene in benzene from the parameters of the ^{19}F NMR spectrum on the basis of the dependence of $\Delta^*(^{19}F)$ on the concentration of *p*-difluorobenzene (Eqn.11); $a(^{19}F)$ = +2.3 G. The ^{19}F peak shifts downfield, the shift being caused by the direct interaction of the π orbital of oxygen with the *n* orbital of the fluorine atom of the ligand.[16]

Signs of complex formation, namely the paramagnetic shifts of the peaks due to the ^{19}F and ^{13}C nuclei, have also been observed for a number of other organofluorine molecules.[25,26] We may note that no studies have been made of the concentration dependence of the shifts in the above investigations and the HFI constants calculated from the paramagnetic shifts in the pure, undiluted organofluorine liquids were therefore determined incorrectly. For this reason the correlations established by Hamza et al.[26] between the ^{19}F HFI constants

and the solubility of oxygen are erroneous and the conclusions based on these correlations concerning the causes of the high solubility of oxygen are unfounded.

Knowing the equilibrium constants, it is possible to calculate the fraction of oxygen bound in complexes in the solution.[24] Thus 52% of the entire dissolved oxygen is present in complexes in pure C_6F_6 at 40 °C, while in pure compound 2 (Table 5) 41% is bound under the same conditions; in compound 3 the proportion of oxygen bound in the complex with the CF_3 group is 37% and, when account is taken of all the fluorine-containing groups (CF_3 and CF_2), the proportion is 65%. We may note that the solubility of oxygen in organofluorine liquids exceeds on average its solubility in proton-containing analogues by a factor of 1.5–2. This "excess" oxygen content in organofluorine compounds is approximately consistent with the amount of oxygen incorporated in the complex, i.e. the cause of the anomalous solubility of oxygen in organofluorine compounds is its complex formation reaction.

V. OXYGEN COMPLEXES IN CHEMICAL REACTIONS

The question of the role of complexes in chemical reactions has no unambiguous solution; complex formation by no means always ensures the molecular organisation of the chemical reaction and frequently inactivates the reactants and inhibits the reactions.

Molecular oxygen is active in radical-chain reactions and its activity masks the chemical behaviour of its complexes. The contribution of chemical processes in which the complexes are detected or manifested can therefore be isolated only on rare occasions.

The photochemical oxidation of specially purified ethanol by molecular oxygen has been studied.[27] Solutions of oxygen in ethanol were irradiated with light corresponding to the absorption band, which appeared only in the presence of oxygen. It was found from the difference between the electronic absorption spectra of ethanol saturated with nitrogen and oxygen and was attributed to the oxygen complexes. This band lies in the range 2170–2700 Å and the intrinsic absorption of alcohol begins only at $\lambda < 2200$ Å. On irradiation with light at $\lambda > 2400$ Å, which is absorbed only by the complexes, oxygen was absorbed and oxidation products were formed. Both the kinetics of the consumption of oxygen and the composition of the products were typical for autocatalytic oxidation: the acceleration of the consumption of O_2 in time was observed and the yields of hydrogen peroxide and acetaldehyde (in comparable amounts) pass through a maximum, which is typical for intermediate products, while the yield of acetic acid (the final product) increased monotonically and reached a limit.

The oxidation was apparently initiated by the absorption of light by the oxygen complex (possibly with formation of the radicals $CH_3CH_2\dot{O}$ and $H\dot{O}_2$ or $CH_3\dot{C}HOH$ and $H\dot{O}_2$ as a result of the primary electron transfer in the excited complex and subsequent proton transfer). The disproportionation of the radicals in the primary pair can ensure comparable yields of CH_3CHO and H_2O_2 (as has been observed experimentally[27]). The subsequent consumption of these products cannot be accounted for unambiguously. It can be associated either with the fact that the oxidation is a chain process (possibly even with short chains) or the fact that oxygen also forms complexes with CH_3CHO and H_2O_2, which are involved in further photoinduced reactions. Experimental data do not so far permit unambiguous answers, but the conclusion that the complexes of O_2 with organic molecules initiate the photoinduced oxidation is entirely reliable.

The rules governing the autoxidation of organoelemental compounds also make it necessary to adopt the hypothesis of the formation of an oxygen complex as the first stage in the oxidation process. The presence of this stage has been justified experimentally in the oxidation of diethylcadmium;[28] the oxygen complex is transformed further into organoelemental peroxide compounds.

The behaviour of the O_2 + trimethylboron system has been subjected to a quantum-chemical analysis.[29] The geometrical parameters of the system and the orientation of the interacting species are illustrated in Fig.7. As the species approach one another to a distance $r \leq 3.5$ Å, their energetically favourable orientations are grouped near the C_3 symmetry axis of the trimethylboron molecule, i.e. oxygen tends to "stick" to the boron atom. As the O_2 molecule moves along the z axis on the potential energy surface, there is a local minimum corresponding to an intermediate complex in a triplet state (complex A), whose coordinates are $r = 2.25$ Å, $\gamma = 100°$, and $\alpha = 0$. It is subsequently transformed into another complex with the coordinates $r = 1.65$ Å, $\gamma = 102°$, and $\alpha = 90°$ in a triplet state (complex B).

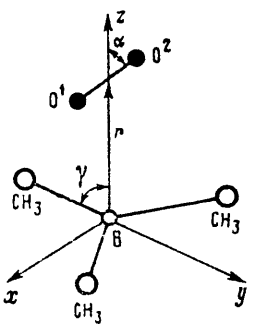


Figure 7. The geometrical parameters of the O_2 + trimethylboron system.[29]

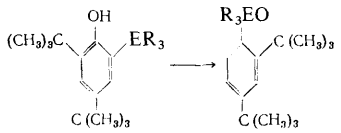
For the singlet state of the system, there is one minimum on the potential energy surface (whose coordinates are $r = 1.60$ Å, $\gamma = 102°$, and $\alpha = 90°$) and the transfer of complex B to this minimum hardly requires a change in energy and is accompanied by a redistribution of electron density.

On moving along the reaction coordinate, electron density is transferred from the O_2 molecule to the other species involved, the strength of the O–O bond in the O_2 molecule diminishes (mainly as a result of the loosening of the π-bond), and the B...O_2 bond formed has σ character. One of the B–CH_3 bonds is weakened and oxygen is inserted with formation of $(CH_3)_2BOOCH_3$. It has been suggested that the primary peroxides, whose subsequent decomposition initiates the chain oxidation of the organometallic compound, are formed via this pathway.

A minimum on the potential energy surface has also been predicted theoretically for the complexes of O_2 with benzene, pyrrole, and aniline, where O_2 is located above the plane of the molecules, the depth of the minimum being independent of the mutual orientations of the interacting species and the equilibrium distance at the minimum is approximately 3 Å, while the charge is transferred from the aromatic molecule to O_2.[30] It is difficult to say anything definite about the reliability of these results.

Finally one should note the influence of oxygen on the isomerisation of organoelemental phenols.[8] In the absence

of oxygen, shielded phenols (Table 1) are stable, but in the presence of O_2 they rearrange to ethers, for example:



;

E = Si, Ge .

Oxidation products are not then observed, which makes it necessary to assume that the rearrangement takes place in the complex of molecular O_2 with phenol. A correlation has actually been found between the stability of phenols with respect to the rearrangement and the complex formation constants K determined from the quenching of the luminescence (Table 1): the higher the value of K, the easier the rearrangement of the phenol.

The complex formation reaction with oxygen is probably important in the initiation of oxidation processes, especially in the atmosphere (in particular in the decomposition of Freons). Nor can one rule out the involvement of the complexes in steps where oxygen adds to radicals in kinetic chain propagation reactions.

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Many spectroscopic features (the removal of spin prohibitions, the appearance of new absorption bands, and the quenching of excited states) indicate the formation of complexes between molecular oxygen and organic molecules. However, the most reliable criteria and evidence for complex formation are the paramagnetic shifts of the NMR peaks and their temperature and concentration dependences. They demonstrate unambiguously that the formation of normal, equilibrium complexes constitutes the main and "strongest" intermolecular interaction in the oxygen–organic molecule pair. This is accompanied by the combination of the electron clouds of the interacting species and the partial transfer of unpaired electrons from oxygen to the ligand. The equilibrium constants and the fraction of spin density transferred have been determined for a number of organic molecules and even the energy has been estimated for some of them.

The n orbitals of oxygen (they give rise to complexes of the $n-\sigma$ type) and the π orbitals (giving rise to complexes of the $\pi-\sigma$, $\pi-n$, and $\pi-\pi$ types) participate in complex formation, the π-complexes predominating.

A number of examples indicating the involvement of the oxygen complexes in chemical reactions were examined above. However, one can assume that their importance in chemistry is much wider. The oxidation of polyconjugated aromatic molecules to endoperoxides and the oxidation of polyene hydrocarbons (β-carotene, retinal, and vitamin A) and polymers (polyacetylene) apparently proceeds via $\pi-\pi$ complexes. The oxygen $\pi-\sigma$ complexes lie on the coordinate of the RH + O_2 → $\dot{R}$ + $H\dot{O}_2$ reaction, which ensures the initial chain initiation in chain oxidation processes. Their role is also important in the photoinitiation of oxidation processes, because the complexes exhibit an intrinsic optical absorption. These processes are particularly significant in the chemistry of the atmosphere in connection with the danger of the breakdown of the ozone layer by Freons. The formation of complexes between Freons and oxygen and their photodissociation can prove to be important elements of the mechanism of the decomposition of Freons in the atmosphere and they must be taken into account in modelling chemical-ecological phenomena.

There is little doubt that elementary photophysical processes involving the oxygen-induced quenching of the excited states and sensitisation (deactivation, energy transfer, the removal of spin prohibitions, and the change in spin multiplicity) are induced precisely in the complexes and that the exchange-resonance mechanisms of these processes operate in the latter.

Finally, the formation of complexes by molecular oxygen has so far been only slightly investigated; there is little information about the structure and dynamics of the complexes, about their reactivity, and about their role in chemical reactions of oxygen. This applies particularly to the complexes of oxygen with organoelemental molecules, among which a special place belongs to the oxygen complexes of organofluorine derivatives. Much remains obscure and contradictory concerning the formation of complexes between oxygen and aromatic molecules and concerning the way in which the interacting species are "joined together" in the complex.

However, the considerable progress achieved in this field during the last three–five years must be noted: until then, nothing definite whatsoever was known about the oxygen complexes (apart from certain assumptions and guesses). This progress is due to the development of new ideas and approaches (in particular the application of nuclear magnetic resonance) for the solution of complex formation problems. It is evident that the ideas and approaches developed can be used also to investigate the complexes of oxygen with inorganic molecules, for the solution of the problems of the activation of oxygen, in the search for and synthesis of molecular oxygen transporting agents, etc.

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The Orientation of Nematic Liquid Crystals

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The methods for the homeotropic, filted, and homogeneous alignment of nematic liquid crystals on solid supports are examined. A systematic account is given of the literature on chemical orientation agents and methods for the formation of anisotropic orienting surfaces. The physicochemical and anisotropic-elastic mechanisms of the alignment of liquid crystals on solid supports are discussed.
The bibliography includes 225 references.

CONTENTS

I.	Introduction	129
II.	Characteristics of the alignment of nematic liquid crystals	129
III.	Chemical orienting agents	130
IV.	Anisotropic orienting coatings	133
V.	The mechanisms of the orienting effect of the surface	135
VI.	Examples of the preparation and applications of aligned nematic liquid crystals	138

I. INTRODUCTION

The studies of Frederiks and Tsbetkov,[1,2] carried out in our country during the 1930's, attracted the attention of investigators to the liquid crystal state of matter and recent advances in microelectronics have made it possible to employ the unique properties of liquid crystals in practice. Fields associated with the investigation and development of information-reproducing devices employing electro-optical effects in nematic liquid crystals (NLC) are developing particularly vigorously.

The study of the alignment (orientation) of the NLC on solid surfaces is of great interest for both theoretical research into the physical chemistry of surfaces and for the application of electro-optical effects in the technology of the preparation of liquid crystal displays. The orientation methods depended for a long time on the experimenter's art and skill and only recently have become available for industrial use as a consequence of intense investigations, which have been described in a number of reviews.[3-7]

In recent years the number of studies devoted to this problem has continued to grow. Research is being prosecuted in the following main fields: the development of new technological procedures and chemical agents for the alignment of NLC; the study of the mechanism of the orienting effect of the surface; the optimisation of the orientation parameters in liquid crystal devices. An attempt has therefore been made in the present review to give an up-to-date description of the methods and mechanisms of orientation with allowance for the influence of the latter on the electro-optical characteristics of NLC.

II. CHARACTERISTICS OF THE ALIGNMENT OF NEMATIC LIQUID CRYSTALS

(a) The NLC Director

The macroscopic state of NLC is characterised by the direction of the preferential orientation of the long molecular "axis" which is called the director. The intermolecular interaction of the liquid crystal material with the solid surface can lead to different positions of the director relative to the support. Depending on the angle ϕ between the director and the normal to the surface (Fig.1), the following types of alignment are distinguished: homeotropic ($\phi = 0$), tilted ($0 < \phi < \pi/2$), and planar ($\phi = \pi/2$). The homogeneous (planar or tilted) alignment, where the NLC molecules are arranged almost parallel to a specific direction, i.e. have a constant azimuthal angle α,† is a special case of the alignment of NLC most frequently used in indicator devices.

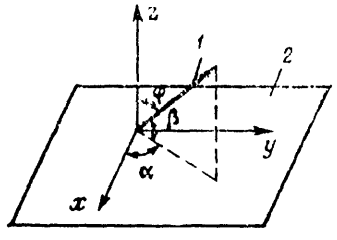


Figure 1. Alignment of the NLC director (line *1*) relative to the plane of the support (line *2*).

(b) The Energy of the Anchoring of NLC to the Support

An important characteristic of the interaction of NLC molecules with the surface is the energy of anchoring to the surface, defined as the energy which must be consumed to rotate the director from the equilibrium position by a certain angle. Two quantities are distinguished, one of which (W_1), corresponds to the rotation of the director by an angle $\Delta\phi$ in a plane perpendicular to that of the support and the other (W_2) corresponds to the rotation by an angle $\Delta\alpha$ in the azimuthal plane xy. The dependence of the anchoring energy on the angle of rotation of the director is represented by the phenomenological formulae[6] $W_1 = W_\phi \sin^2 \Delta\phi$ and

† Henceforth we shall assume throughout that this direction coincides with that of the x axis, i.e. $\alpha = 0$.

$W_2 = W_\alpha \sin^2 \Delta\alpha$, where W_ϕ and W_α are the polar and azimuthal anchoring energies corresponding to the rotation of the director from the initial position by angles $\phi = \pi/2$ and $\alpha = \pi/2$ respectively.

In the terminology of physical chemistry of surfaces, the anchoring energy W_ϕ can be represented as the difference between the energies of the interfacial NLC–solid support interaction γ_{LS} for the planar and homeotropic alignments: $W_\phi = \gamma_{LS}(\pi/2) - \gamma_{LS}(0)$. The interfacial energy can be expressed in its turn in terms of the surface energies of both phases at the interface with a vacuum (γ_L and γ_S):[8]

$$\gamma_{LS} = \gamma_S + \gamma_L - W_a, \quad (1)$$

where W_a is the energy of adhesion of the NLC to the support.

If the energy of the interaction of the NLC molecule with the surface of the support is sufficiently large and determines a particular direction of the director relative to the surface which does not change under the influence of external fields (i.e. the energies W_ϕ, $W_\alpha \to \infty$), then such a case is referred to as strong anchoring. On the other hand, if an electric or magnetic field can break down the order on the surface (W_ϕ and W_α are finite), then the anchoring is regarded as weak.[9]

III. CHEMICAL ORIENTING AGENTS

In the formation of homogeneously aligned NLC specimens, it is necessary to take into account the chemical nature of both the liquid crystal material and of the solid surface. In research and technological developments NLC belonging to the classes of Schiff bases, azobenzenes, azoxybenzenes, phenyl benzoates, cyanobiphenyls, phenylcyclohexanes, and their derivatives are used most frequently.[10] The surface of the supports used in liquid crystal devices is as a rule inhomogeneous and contains sections consisting of glass and a conducting film (usually indium or tin oxide). The chemical structure of the support can be modified in various ways in order to impart to it the required surface properties: as a result of the influence of external factors (temperature, chemical medium); by the adsorption of a monolayer of a surfactant; by depositing a special orienting layer with the required surface structure.

1. The Alignment of NLC on Glass and Oxide Films

The majority of clean oxide surfaces promote the planar alignment of NLC.[7,11–14] The homeotropic alignment observed on freshly sputtered In_2O_3, SnO_2, ZrO_2, Al_2O_3, and MgO films[13–18] for Schiff base and cyanobiphenyl NLC can be accounted for by the effect of amphiphilic impurities present in them as a result of the partial degradation of the NLC.[13]

The influence of external factors on the chemical structure and orienting properties of the surface can be traced in relation to a glass support. The glass surface contains mainly the siloxane $\geqslant$Si–O–Si$\leqslant$ and silanol $\geqslant$Si–OH groups, whose number is determined by the previous history of the glass. The cleaning of supports by etching in acid and peroxide solutions converts the siloxane groups into silanol group and promotes the homeotropic alignment of the NLC molecules with polar end groups.[18–21] On the other hand, etching of the supports in alkalis or annealing at an elevated temperature, particularly *in vacuo*, entails the conversion of the silanol groups into siloxane groups and homeotropic alignment is not observed even for NLC with polar groups at either end of the molecule.[21]

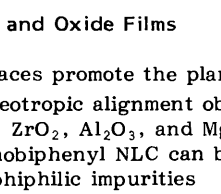
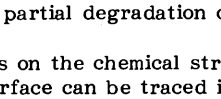
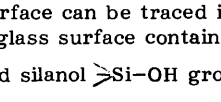
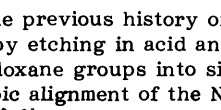
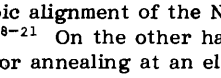
Chemical cleaning of the surface proved to be one of the first methods for the preparation of homogeneously aligned specimens,[17–21] but, as a result of the marked dependence of the type of alignment on the nature of the NLC[13,14] and poor reproducibility, it is hardly used nowadays.

2. The Orienting Effect of Surfactants

(a) Surfactant Additives in a Liquid Crystal Material

After the observation of the homeotropic alignment of *p*-methoxybenzylidene-*p'*-n-butylaniline (MBBA—one of the classical objects in studies on NLC) following the addition to the latter of small amounts (0.5 wt.%) of a polyamide resin,[22,23] a large number of additives with an analogous effect also on other types of NLC were proposed (Table 1). Many fewer additives have been proposed for the attainment of the planar alignment of NLC; these include dicarboxylic acids,[37] diazopolyoxycycloalkanes, diazopolyoxydicycloalkanes,[57] and aromatic ethers with an NLC structure.[58]

Table 1. The surfactants used for the homeotropic alignment of NLC.

Surfactant	NLC*	References
Polyamide resins and cellulose esters	SB	22–24
Lecithins	MBBA, CBP, PB, AOB	7, 25–32
Aliphatic amines $C_nH_{2n+1}NH_2$, $n \geqslant 12$	SB	31–34
Nitriles $C_nH_{2n+1}CN$, $n \geqslant 7$	SB, AB, AOB, PB	34
Esters $C_nH_{2n+1}COOC_mH_{2m+1}$, $n = 11$, $m = 6$; $n = 1$, $m = 1$–18	SB, AB, AOB, PB	34, 35
Alcohols $C_nH_{2n+1}OH$, $n = 1$–20	SB	36, 37
Aromatic amines and phenols: *N*-isopropyl-*N*-phenyl-*p*-phenylenediamine, β-naphthylphenylamine, *p*-hydroxyphenyl-β-naphthylamine, 2,6-di(t-butyl)-4-methylphenol, hydroquinone, 4-t-butylcatechol, 2-t-butoxyanisole	SB	38
Tetracyanodiphenodimethane, tetracyanonaphthoquinodimethane, and their derivatives	NLC with $\Delta\epsilon^{**} < 0$	39, 40
Alkylammonium salts $(C_{16}H_{37})_2(CH_3)_2\overset{+}{N}B(C_6H_5)_4^-$; $[C_nH_{2n+1}N(CH_3)_3]^+X^-$, $n = 1$–16, X = Hal; $(C_nH_{2n+1})_4N^+X^-$, $n = 1, 4, 6$, X = Hal	SB, AOB, PB, PCH	23, 30–32, 41–48
N-Alkylpyridinium salts: $n = 12, 14, 16$; X = Cl, Br, I	SB, PB	46, 47
Carboxylic acids: $C_nH_{2n+1}COOH$, $n > 10$; $C_{18}H_{37}CH{=}CH(CH_2)_7COOH$;     $C_{16}H_{33}O$	SB, PB, AB, AOB, CBP	34, 35, 49
Carboxylatochromium complexes:  X = Hal, NO_3	SB, CBP, AOB	50, 54
Tributyltin oxide and chloride	SB	53, 54
Fluorine-containing surfactants: $C_6F_{13}SO_3K$; $C_nF_{2n+1}Si(OR)_3$, $n = 4$–8, $R = CH_3$, C_2H_5; $C_nF_{2n+1}SO_2NRC_2H_4N^+(R^1)_2X^-$; $C_nF_{2n+1}SO_2NRC_2H_4N(R^1)_2 \cdot HX$; $C_nF_{2n+1}CONR(CH_2)_lN^+(R^1)_3X^-$; $C_nF_{2n+1}CONR(CH_2)_lN(R^1)_2 \cdot HX$, $n = 5$–10, $l = 1$–5; X = acid group, R, R^1 = lower alkyls	SB, PB	31, 32, 55, 56

*Here and henceforth SB = Schiff bases, CPB = cyanobiphenyls, PB = phenyl benzoates, AOB = azoxybenzenes, AB = azobenzenes, PCH = phenylcyclohexanes.

**The anisotropy of the dielectric constant of the NLC.

The mechanism of this type of alignment is based on the fact that the surfactant molecules present in the liquid crystal material as additives are adsorbed on the surface of the support after coming into contact with it and alter the energy of the interface, promoting a specific type of alignment of the NLC.

The concentration of the additive selected is usually in the range 0.1–2 wt.%. A smaller amount may not have a sufficient orienting effect, a larger amount reduces the temperature range for the existance of the mesophase, while ionic surfactants cause in addition an appreciable increase of the conductivity of the NLC, which is undesirable for NLC indicators based on field effects. A disadvantage of this method of aligning NLC is a decrease of the concentration of the adsorbed surfactant molecules going from the filling orifice of the indicator to its periphery, which leads to a non-uniformity of the alignment of the NLC. Account must be taken of the fact that the surfactants entering the NLC from adhesives and substances used to make a hermetic seal[59] or the impurities in the NLC and its decomposition products[13,14] may exert an undesirable orienting influence in the preparation of liquid crystal indicators.

(b) Deposition of a Surfactant Film on the Support

The majority of the surfactants described above can be deposited directly on the support by adsorption from solutions or by the Langmuir–Blodgett method. The structure of the surfactant monolayers and the alignment of the NLC on the latter depend on the density of the molecules adsorbed on the surface.[7,27] Thus, when hexadecyltrimethylammonium bromide is used, an increase of its molecular density on glass results in the replacement of the planar alignment of MBBA by its homeotropic alignment;[44,45] the homeotropic alignment of cyanobiphenyls and azoxybenzenes is achieved only at a specific concentration of stearatochromium chloride, used to treat the support;[60] on the other hand, the orienting influence of lecithin is impaired by increased packing density of its molecules on the surface.[27,28]

Surfactants containing long alkyl groups, for example, barium stearate,[42] the aliphatic monoamines $C_nH_{2n+1}NH_2$ (n = 12 to 16),[31–33] and fluoro-derivatives of various types with a C_nF_{2n+1} (n = 5–10) end group[55,66] are used as a rule to achieve the homeotropic alignment of NLC. The length of the hydrocarbon group affects the surface energy of the surfactant film and hence the alignment of the NLC. Thus, when the number of carbon atoms is changed from 10 to 6 in aliphatic monoamines, the angle of tilt of the MBBA director to the surface β (see Fig. 1) diminishes from 78° to 30°.[33] The molecules of surfactants proposed for the attainment of a planar alignment frequently contain not less than two polar end groups capable of being adsorbed on the surface.[37,61,62]

Orienting surfactants are usually deposited on the support from organic or aqueous solutions, but other methods can also be employed. For example, on films deposited from a gas discharge in metal alkoxide vapours, a homeotropic alignment of NLC has been observed for quadrivalent metals and a planar alignment for tervalent metals.[63]

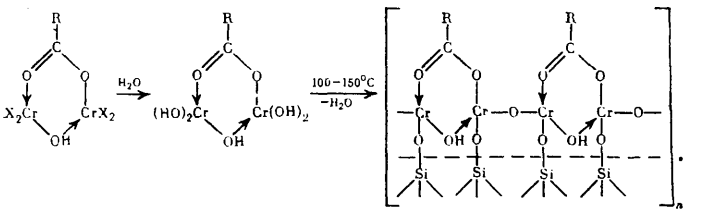
The structure of the NLC molecules themselves also plays a major role. In contrast to the majority of other classes of compounds, azoxybenzenes are not aligned homeotropically on surfaces covered by lecithin,[28] while cyanobiphenyls are not aligned in a planar manner on films of dicarboxylatochromium complexes.[64]

The surfactant monolayers physically adsorbed on the surface are unstable with time: the interaction of the polar groups of the NLC or impurities with surfactant molecules can alter the structure of the orienting layer and lead to breakdown of orientation.

(c) The C emisorption of Surfactants by the Surface of the Support

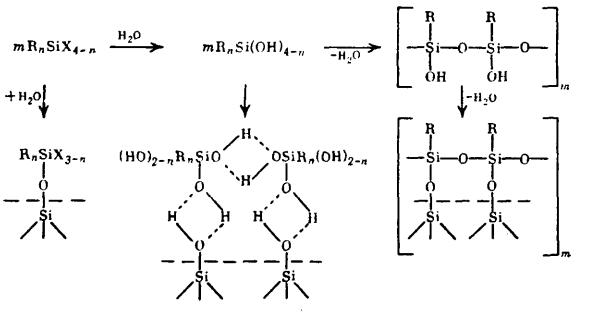
In order to improve the stability of the alignment of NLC, it has been suggested that one use surfactants which bind chemically to the support as a result of the interaction with the surface hydroxy-groups. It has been reported that the replacement of the silanol groups on the surface of silica by alkoxy-groups at elevated temperatures when amines are used as catalysts makes it possible to obtain a stable homeotropic alignment of many NLC.[36,37] However, this method is apparently very sensitive to the number of silanol groups, because it was impossible to reproduce these results in another study.[7]

A stable homeotropic alignment of not only nematic but also cholesteric and smectic liquid crystals is achieved on supports treated with carboxylatochromium complexes, which form hydrogen and siloxane bonds with the atoms in the surface layer of the support:



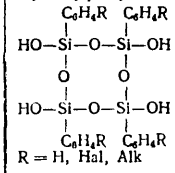
Here R is an aliphatic[50,51] or *o*-phenyl group[52] and X is an anion. On the other hand, organochromium complexes with dicarboxylate ligands are used to achieve a planar alignment.[64]

Alkoxy- and chloro-silanes have been widely investigated and used as orienting surfactants.[3,7,65–67] The increased interest in these substances is due to the effective adhesion and stability of organosilicon films on hydrophilic supports as a result of chemical interaction with the silanol surface groups. The hydrolytic and polycondensation processes occurring both in the solution of R_nSiX_{4-n} and on the surface of the support lead to the formation of a polysiloxane layer:[68]



Silanes can therefore be regarded as both surfactants and as the starting compounds for the deposition of polymer films (see Table 2 below). The supports are usually treated with silanes by immersion, centrifugation, and boiling in aqueous or organic solutions (1–5 wt.%) or in the vapour phase (in the case of volatile silanes).

Table 2. Polymeric materials of the orienting films.

Material of orienting film	Method of deposition	Starting materials	References
	Homeotropic alignment of NLC		
Polysiloxanes	Polymerisation in glow discharge	Hexamethyldisiloxane, trimethylvinylsilane	75, 76
"	Cathodic sputtering	Tetraethoxysilane	63
"	From organic solutions	Silicone liquids	77, 78
Compositions based on organosilicon and organotitanium cpds.	From organic solutions	$C_nH_{2n+1}Si(OC_2H_5)_3$ + $Ti(OC_4H_9)_4$, n = 16–18	71, 72
Fluorinated polymers	Cathodic sputtering	Polytetrafluoroethylene	76
Ditto	Polymerisation in plasma	Tetrafluoroethylene, perfluorocyclohexene, perfluorodimethylcyclobutane, perfluoro-1,3-dimethylcyclohexane	79–83
	Homogeneous alignment of NLC		
Polyisobutene	Polymerisation in plasma	Isobutene	76
Polybutadiene	From polymer solution	Butadiene	7
Polystyrene, copolymers with divinylbenzene	From polymer solution	Polystyrene, polystyrene plus divinylbenzene	84
Poly-*p*-xylylene and its derivatives	Pyrolysis with subsequent condensation on a support	CH_2–C_6H_4–CH_2 | | CH_2–C_6H_4–CH_2	37, 84, 85
Poly(vinyl alcohol) (PVA) and its derivatives	From aqueous solutions	Poly(vinyl alcohol)	86–88
Polyoxyethylenes	—	$CH_3(CH_2)_{15}(OC_2H_4)_{20}OH$	37, 86
Polyacrylates	From polymer solution	Polyacrylate, polycyanoacrylate, polyacrylonitrile plus PVA	7, 89, 90
"	Polymerisation in plasma	Methyl methacrylate	84
Polyesters, polyurethanes, polysulphones	From polymer solution	Polyesters, polyurethanes, polysulphones	7, 87
Cellulose resins	From organic solutions	Methylcellulose, nitrocellulose acetylcellulose, cellulose acetate butyrate	91–93
Polyoxazole, polythiazole, polyoxazinol, polyoxazinediol, polydiquinoxaline	From organic solutions	Isophthaloyl chloride plus 3,3'-dihydroxybenzidine in *N*-methylpyrrolidinone	94
Polyimides and their copolymers with epoxide and organosilicon resins	From organic solutions of polyamidoacids with subsequent imidisation	Polyamidoacids	95–111
Polysiloxanes and compositions containing them together with Ti, Al, Sn, Ce, etc compounds	From solutions of hydrolysable compounds	$Si(OR)_4$, $R^1Si(OR)_3$, R = CH_3, C_2H_5; R^1 = C_6H_5; CH_2 = CH; $Ti(OC_4H_9)_4$; $AlCl_3$	69, 73, 74, 76, 112–120
Ditto	Polymerisation in plasma	Methylsiloxane	84
"	From polymer solution	Polymethylphenylsiloxane	7
Silsesquioxanes	From organic solutions, sputtering	 R = H, Hal, Alk	121
Fluorinated polymers	Vacuum sputtering	Polytetrafluoroethylene	87
Ditto	Sliding contact	Poly(vinyl fluoride)	24, 42
Poly (vinylpyridinium bromides)	From aqueous solution	Poly(2-methyl-5-vinylpyridylbutyl bromide)	46
Poly-γ-methyl-*L*-glutamate	—	—	122

In order to achieve a homeotropic alignment, alkoxy- and chloro-silanes with long alkyl or fluoroalkyl chains are used, for example $[C_nH_{2n+1}(CH_3)_2N(CH_2)_3Si(OCH_3)_3]^+Cl$ with n = 12–18,[3,31,32,65] $C_{18}H_{37}SiCl_3$,[7,42] and $C_nF_{2n+1}Si(OR)_3$ with n = 4–8.[56] Organosilicon compounds which promote a planar alignment of NLC contain as a rule a group with a ring structure (phenyl, biphenyl, or cyclohexyl groups)[7,66,69] or a hydrocarbon chain capable of binding via several groups to the support, for example, $CH_3OOCCH_2NHNH(CH_2)_nNH.(CH_2)_mSi(OC_2H_5)_3$ with n = 2, 3 and m = 2–5[70] or $CH_3NH.(CH_2)_3Si(OCH_3)_3$.[3,65]

One must note that, owing to the marked dependence of the quality of the orienting surfactant film on the preparation of the surface, an inhomogeneity in the orientation of the NLC may be observed on plates with an electrode pattern. This disadvantage is eliminated by introducing surfactants into film-forming solutions based on hydrolysable compounds, such as, for example, $Si(OC_2H_5)_4$, $Ti(OC_4H_9)_4$, or $AlCl_3$.[71–74] The polymer coatings formed adhere strongly to both the glass and to the electrode film, playing at the same time the role of a protective dielectric layer.

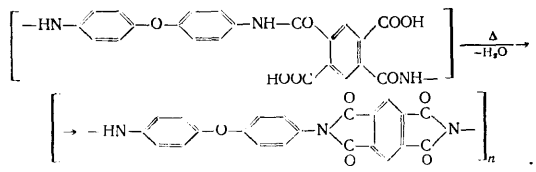
Orienting surfactants forming chemical bonds with the support are nowadays widely used in the technology of the manufacture of liquid crystal devices, particularly with an initial homeotropic alignment. However, their use is not always compatible with the formation of a hermetic seal for the indicators by means of a glass frit because the thermal stability of surfactant films is comparatively low (usually up to not more than 200 °C).

3. Orienting Polymer Coatings

In order to create surfaces with specific physicochemical properties, polymer films obtained by a wide variety of methods are frequently used. With the exception of certain polymers, proposed to achieve a homeotropic alignment of NLC, most of them orient NLC homogeneously after mechanical rubbing (Table 2). The conditions in the deposition of the polymer have a considerable influence on its orienting properties. For example, the homeotropic and planar alignments of MBBA on polytetrafluoroethylene films, deposited respectively by cathodic sputtering[76] and by means of a sliding contact,[42] have been reported. The method involving deposition from solutions of compounds which undergo hydrolysis and polycondensation has interesting possibilities in this connection. The wide-scale application of this procedure (see, for example, the relevant patents[71–74,112–120]) can be explained by the fact that, by selecting the heat treatment temperature and by mixing in various proportions silicon, titanium, aluminium, tin, cerium, zinc, etc. compounds, it is possible to alter the chemical structure of the surface, achieving thereby a homeotropic or planar alignment of the NLC and at the same time one can regulate the optical and dielectric properties of the orienting films.

Among the multiplicity of materials listed in Table 2, poly(vinyl alcohol) (PVA) layers and polyimide films are most widely employed. The ready availability of PVA films, the simplicity of their deposition, and their effective adhesion to glass and oxide surfaces have led to their extensive application in laboratory practice. However, their unsatisfactory dielectric characteristics, low thermal stability (up to not above 180 °C), and the loss of their orienting capacity under the influence of moisture frequently prevent their application in industrial technology.

Polyimide films have a high breakdown potential and a very high thermal stability (up to 450 °C), which makes it possible, in particular, to achieve a hermetic seal for indicators with the aid of readily fusible glass. Polyimide films are obtained by the thermal dehydrocyclisation of polyamidoacids, which are deposited on the support by centrifugation or by immersion in an organic solution; a 5–10 wt.% solution of polypyromellitamido-acid in dimethylformamide (DMF) is used as a rule.[103] The heat treatment of the films must be carried out in at least two stages: at 80–100 °C the solvent is removed from the layer and at 300° to 400 °C the imidisation process proper takes place:



The main disadvantage of polyimide films is the reduction of the effectiveness of adhesion under the influence of moisture. In order to improve the adhesion of the orienting coating to glass, it has been suggested that the surface of the support be modified with organosilicon compounds having the formula R_nSix_{4-n} [104] or that a sublayer of an inorganic material[123,124] or an epoxide resin[125] be deposited. An increased resistance of polyimides to moisture can also be attained by copolymerising them with organosilicon[107,111] and epoxide compounds.[108,109]

A new promising trend in the formation of liquid crystal devices, involving the employment of plastic supports instead of glass supports, has been established in recent years.[126,127] In this connection publications devoted to the selection of chemical orientation agents for such surfaces have appeared. Thus it has been suggested that an orienting PVA film[127] or mixed alkylalkoxy-derivatives of titanium and aluminium[128,129] be deposited on a poly(ethylene terephthalate) support.

4. The Polar Energy of the Achoring of the NLC to the Support

The structure of the surface determines not only the direction of alignment of NLC molecules but also the energy of their anchoring to the support. This quantity has a significant influence on the behaviour of the NLC layer in electric and magnetic fields[9] and information about its estimation and about the possibility of its regulation is therefore important. It has been suggested that the bonding energy with the surface in the case of weak anchoring be determined qualitatively from the dimensions of different alignment defects,[33] from the critical field in the deformation of the NLC layer by magnetic[31,32] or electric[29,132,133] fields, or from the extent of double refraction.[134,135] It must be emphasised that reliable methods for the measurement of the anchoring energy are so far lacking and the values quoted in the literature are merely estimates.

The influence of chemical orienting agents on the polar energy of the anchoring of the NLC to a solid surface W_ϕ is illustrated in Table 3, which lists the few experimental and theoretical estimates available in the literature. The dependence of W_ϕ on the length of the hydrocarbon group, the type of the polar group in the surfactant molecules, and the nature of the support has been investigated.[31,32] It has been shown that, with increase of the length of the alkyl group of the orienting surfactant, the anchoring energy initially increases and then falls; in the homologous series $[C_nH_{2n+1}(CH_3)_2N(CH_2)_3Si(OCH_3)_3]^+Cl^-$ the maximum value of W_ϕ is attained for n = 14–16. It has also been noted that the use of cationic surfactants leads to a higher value of W_ϕ than in the case of non-ionic alkylamines and amphoteric lecithin, the energy of anchoring the NLC to glass being almost a factor of two smaller for the same surfactant than the energy of anchoring to indium oxide. Thus the polar energy of anchoring the NLC to a solid surface is evidently determined by steric, dispersion, and polar factors.

IV. ANISOTROPIC ORIENTING COATINGS

In order to produce liquid crystal specimens with a homogeneous (planar or tilted) alignment, it is insufficient to ensure the distribution of NLC molecules at a specific angle relative to the surface of the support; it is also necessary to impart anisotropic properties to the surface, so that, on interaction with the latter, the NLC molecules are "built in" along one specified direction. For this purpose, one usually employs supports with a definite surface relief (as a rule in the form of grooves and humps) and also films with an ordered molecular structure.

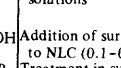
Table 3. The polar energies of the anchoring of NLC to orienting surfaces.

Orienting surface	NLC	φ, °	W_ψ, mJ m^{-2}	References
Glass	PAA†	90	0.36*	[136]
Heated paper decomposition products	MBBA	0	10^{-4}	[130]
Lecithin	MBBA	0	$(1–3)\cdot10^{-3}$	[25, 31, 32]
Lecithin on rubbed surface	AOB + PB	6	$9\cdot10^{-3}$	[29]
Aliphatic acid derivatives on polished glass	MBBA	$\geqslant$0	10^{-1}	[133]
$C_{16}H_{33}OH$	MBBA	0	$2.4\cdot10^{-3}$	[32]
$C_nH_{2n+1}NH_2$, n = 14–18	MBBA	0	$(1.2–2.0)\cdot10^{-3}$	[31]
$C_nH_{2n+1}NH_2$, n = 6–12	MBBA	3–24	10^{-4}–10^{-3}	[33]
$C_nH_{2n+1}NH_2$, n = 7	MBBA	35	$(1–5)\cdot10^{-3}$	[31]
$[C_nH_{2n+1}N(CH_3)_3]^+X^-$, X = Cl, n = 10–18	MBBA	0	$(1.0–3.8)\cdot10^{-3}$	[31]
Ditto, X = Br, n = 10–14	MBBA	0	$(2.2–4.5)\cdot10^{-3}$	[31]
Ditto, X = Br, n = 6–8	MBBA	75	10^{-3}	[31]
$C_nH_{2n+1}N^+(CH_3)_2(CH_3)_3Si(OCH_3)_3Cl^-$, n = 10–18	MBBA	0	$(0.3–1.3)\cdot10^{-2}$	[31, 137, 138]
$C_8F_{17}SO_2NH(CH_2)_3N^+(CH_3)_3I^-$	MBBA	0	$(1.0–2.7)\cdot10^{-2}$**	[138]
Ditto	MBBA	0	$(3.0–5.0)\cdot10^{-3}$	[1, 137, 138]
SnO_2	MBBA	0	$2\cdot10^{-3}$	[132]
SiO_x**	MBBA	60	10^{-4}	[131]
SiO_x***	CBP	60	$2.1\cdot10^{-3}$	[134]
Free NC surface	MBBA	15	$4.5\cdot10^{-2}$*	[32]
Ditto	CBP	0	$5\cdot10^{-3}$	[32]

*Calculated values.
**Oblique spluttering; the angle between the beam and the surface of the support $\psi < 5°$.
***Double oblique sputtering, initially with $\psi = 30°$ and then with $\psi = 5°$.
† *p*-Azoxyanisole (Ed.of Translation).

The methods used to impart anisotropy to the surface properties of the support in order to achieve various angles of tilt of the director relative to the surface (the angle β, see Fig.1) are given in Table 4. A homogeneous alignment of the NLC parallel to the surface ($\beta = 0$) is observed on inorganic films obtained by "oblique" sputtering at angles ψ between the direction of the stream of particles and the support in the range $15° < \psi < 45$ °C, on surfactant films with an ordered molecular structure, and on photolithographic gratings. Low tilt angles of the director ($0° < \beta < 5$ °) are realised on rubbing the surface, on double oblique sputtering, and on ionic etching of the support; intermediate values of β are achieved on oblique sputtering of silicon or germanium oxide at low angles relative to the surface of the support. Finally, angles β close to 90° are obtained when films which have been rubbed or sputtered on are treated with surfactants used for homeotropic alignment and also as a result of oblique sputtering of Al_2O_3 or CaF_2 on fluorocarbon films polymerised in a plasma and on surfaces treated with surfactants having short alkyl chains.

Table 4. The tilt angles of the NLC director on various orienting surfaces.

Chemical orienting agent	Method of generation of surface anisotropy	NLC	β, °	Method of measurement of β*	Refs.
SiO_x, Au	Sputtering, $\psi = 15-50°$	SB, CBP	0	1, 2, 3	[138–144]
GeO	Sputtering, $\psi = 40-60°$	CBP	0	4	[145]
Bis(*N*-methylamino)-dimethyl silane	Polymerisation in plasma stream, $\psi = 15-70°$	CBP	0±0.5	3,4	[146, 147]
PVA	Transfer of oriented monolayer from surface of water	AOB	0±0.2	5	[148]
SiO_2	Polishing with diamond paste	PB	0.05	1	[149]
Glass	Rubbing	SB	0.5–5	3	[142]
$In_2O_3 + SnO_2$	Rubbing with fabric	PCH	1–4		[151]
In_2O_3	Rubbing	CBP	2.15	1	[150]
SiO_2+$CH_3NH(CH_2)_3Si(OCH_3)_3$	Rubbing with fabric	PB	0.3	1	149
In_2O_3+ polyamideimide	Rubbing with emery paper	PB	0.95	1	[149]
Polyimides	Rubbing	PB	0.11	2	[152]
ditto	Ditto	CPB	0.24	2	[152]
»	»	AOB	0.44	2	[152]
»	»	PCH	0.29–1.20	2	[152]
Polymides	»	PCH	0.35	2	[153]
»	Rubbing on with brushes	AOB	1.0–1.2	5	[148]
PVA	Ditto	AOB	1.1–1.4	5	[148]
SiO_2	Etching with a stream of ions $\psi = 10-30°$	CPB	4	1	[154]
SiO_x	Double sputtering, $\psi_1 = 30°, \psi_2 = 5°$	PB, CBP	0–45	1,4	[155–159]
»	Ditto, $\psi_1 = 5°, \psi_2 = 30°$	SB, CBP	0–30	4	[159]
»	Sputtering, $\psi = 0-20°$	MBBA	15–35	1	[139, 140]
»	» , $\psi = 6-13°$	SB	30–45	3,2	[142, 143]
»	» , $\psi = 5-16°$	CBP	28–41	4	[160]
»	» , $\psi = 5°$	CBP	45		[141]
»	» , $\psi = 5-8°$	CBP	24–29	1,2,6	[7, 161, 143]
»	» , $\psi = 8°$	SB	15–22	1,2	[7, 143]
»	» , $\psi = 4-23°$	MBBA	3–28	—	[162]
GeO	» , $\psi = 5-25°$	CBP	25–28	4	[145, 163]
ditto	Ditto	AOB	28–35	4	[164]
Polytetrafluoroethylene	Polymerisation in plasma on SiO_x films sputtered at an angle $\psi = 30°$	MBBA	87–90	4,5	[83]
ditto	Ditto, $\psi = 5°$	CBP	64	4	[165]
Au	Sputtering on rubbed glass $\psi = 30-45°$	PCH + surfactant	90	5	[166]
$[C_{18}H_{37}N(CH_3)_2(CH_2)_3Si(OCH_3)_3]^+Cl^-$	Treatment in aqueous solution of SiO_x films sputtered at an angle $\psi = 5°$	CBP	74–64	4	[165]
ditto	Ditto	CBP	88–71	4	[167]
»	»	AOB	70–55	4	[165]
»	» , $\psi = 0-30°$	SB, CBP	60–90	1,4	[168]
Lecithin, $RSiX_3$	Treatment in solution of SiO_2, Al_2O_3, and Ti films after ionic etching at an angle of 20–90°	SB	60–90	—	[169]
$RSiX_3$	Treatment in solution of rubbed on In_2O_3 and SiO_2 films	SB	60–90	—	[170, 171]
$C_nH_{2n+1}NH_2$, $n = 6–12$	Treatment in aqueous solutions	MBBA	30–90	4	[33]
	Addition of surfactants to NLC (0.1–0.5%)	MBBA	≲90	—	[38]
$C_nH_{2n+1}OH$, $n = 7–22$	Treatment in surfactant solutions of SiO_2 films after etching with an ionic beam at $\psi = 20°-30°$	SB, PB	75–90	5	[36]
Al_2O_3	Sputtering, $\psi = 0-40°$	CBP, PB	60–90	4	[172]
ditto	» , $\psi = 40-60°$	CBP, PB	≲90	4	[172]
»	» , $\psi = 60-90°$	CBP, PB	90	4	[172]
CaF_2	» , $\psi = 35°$	CBP	15	4	[173]
ditto	» , $\psi = 85°$	CBP	60	4	[173]
»	» , $\psi = 90°$	CBP	90	4	[173]

Methods of measurement of the angle β: 1) magneto-capacitive;[149,150] 2) magnetic with optical recording;[143] 3) capacitive;[158] 4) from conoscopic figures;[160] 5) from extremum phase shift;[174,175] 6) from double refraction.[161]

1. Surfaces with an Orienting Microrelief

One of the commonest methods for the achievement of a homogeneous orientation of NLC involves rubbing the support with a soft fabric, paper, and brushes.[176,177] This method has been modified in a study[178] whose authors suggest that the support be lapped in one direction with diamond paste. The study of the surface by electron microscopy showed that this results in the formation of a system of parallel humps and grooves ~1 μm wide. However, rubbing a chemically inhomogeneous surface can lead to the inhomogeneity of the orientation on different sections of the support with an electrode pattern and to low thermal stability and moisture resistance of the orienting coating. Lapping the protective SiO_2 layer deposited on top of the electrodes makes it possible to obtain a more homogeneous alignment of the NLC with a tilt angle of the director $\beta \approx 0.05°$.[149]

A highly ordered homogeneous alignment on large areas can be achieved by rubbing organic coatings whose surface properties promote a planar alignment of the NLC (see Table 2). The tilt angle of the director achieved on rubbed surfaces depends on the type of NLC, the material of the orienting layer, and the pressure of the rubbing device, varying from 0.2–0.3°[149] to 3–4°.[151]

A multiplicity of other methods have also been proposed recently for the creation of an orienting surface microrelief, for example ionic etching of a dielectric film,[154] scanning with an electron or laser beam,[179] and the use of lithographic procedures.[180–182] However, all these methods are fairly complex for industrial use and, by virtue of its simplicity high productivity and low cost, the rubbing of polymer films therefore remains the most suitable technological method for the attainment of a homogeneous alignment of NLC.

2. Sputtered Inorganic Films

The vacuum sputtering of metals and their oxides and fluorides at low angles relative to the surface of the support results in the formation of a thin film with an anisotropic structure. The suggestion that such films be used for the homogeneous alignment of NLC[183] gave rise to a large number of studies of their orienting capacity.[139–145,155–164,184–190] For example, Au, SiO, GeO, Al_2O_3, MgF_2, CaF_2, as well as other metals, oxides, and fluorides have been tested as materials for the formation of sputtered films; the majority of these orient the NLC molecules in a planar manner with an arbitrary azimuth under the conditions of normal sputtering (sputtering at right angles to the surface?).

The dependence of the surface structure of the sputtered films and of their orienting properties on the angle between the beam and the support during sputtering has been examined in detail in a number of studies.[140,187–190] When the sputtered particles are incident at angles in the range $15° < \psi < 45°$ relative to the support, its surface consists of a system of islands which are extended in the direction at right angles to the plane containing the normal to the surface and the direction of sputtering.[140] Such a surface orients NLC homogeneously, so that $\beta = 0$ and the director coincides with the direction of the long axis of the islands. For $\psi < 15$ °C, the surface relief of the orienting film consists of closely adjacent small asymmetric columns, whose shape and dimensions depend on the material of the film and its thickness; on supports of this kind, NLC molecules are aligned at an angle $\beta = 20–30°$ relative to the plane of incidence of the sputtered particles.[163,187,188]

In order to achieve low tilt angles of the NLC director relative to the surface, it has been suggested that the sputtering process be carried out in two stages: initially at an angle $\psi = 30°$ and then at a very low angle (≲5°) at right angles to the direction of the first sputtering (or in the reverse order).[155–159] Under these conditions, β depends on the thickness of the second layer, which should be very small (~4 Å), since it has been suggested that, in order to

introduce asymmetry along the grooves formed in the first sputtering, it is necessary to deposit individual asymmetric islands and not a continuous film.[156]

It is noteworthy that, in contrast to other fluoride and oxide films, the sputtered CaF_2 [173] and Al_2O_3 [172] films align NLC almost homeotropically with different deviations from $\phi = 0$, depending on the angle of sputtering.

High-frequency plasma reactors can also be used to deposit thin anisotropic films.[79,80,146,147] The homogeneous alignment of NLC with $\beta = 0$ is observed on supports treated at an angle of 50–70° with a stream of plasma containing argon, oxygen, and organosilicon free-radical species.

The principal disadvantage of the vacuum method is the inhomogeneity of the alignment of NLC on supports of comparatively large size owing to the differences between the angles of sputtering for different sections of the plate. In view of the difficulty of achieving low tilt angles of the director, the method of oblique sputtering is used most frequently only in the preparation of indicator devices of small size working under static conditions in those cases where a high thermal stability and moisture resistance of the orienting layers is required.

3. Surfactant Films with an Ordered Molecular Structure

The surfactant films formed on withdrawing the supports from solutions by the Langmuir–Blodgett method can have anisotropic surface properties as a result of an ordered molecular structure and can align NLC homogeneously with the angle of tilt of the director $\beta = 0$. Polymer molecules of extended shape, capable of binding chemically to the support, have been reported to be surfactants of this type: PVA,[191] polymethylsiloxane,[84] and poly(2-methyl-5-vinylpyridiniabutyl) bromide.[46]

In the presence of a dichroic dye, the layers of organic polymers with molecules arranged in such a way that their long axes are almost parallel to one another, possess not only orienting but also polarising properties and can be used as internal polaroids in liquid crystal indicators. Thus the anisotropy of the surface and optical properties of PVA layers with a dye is achieved by directional withdrawal from solution or by shear deformation with the aid of a scraper.[192,193] An orienting polarising film is also formed when a gel of a dichroic dye is deposited with subsequent centrifugation or mechanical deformation of the layer parallel to the surface of the support with the aid of an auxillary plate.[194] The use of internal polaroids does not as yet allow the attainment of a high degree of polarisation of light and a homogeneous alignment of the NLC on supports of a large area but nevertheless it leads to the possibility of simplifying the design of the display and the protection of the polaroids against the unfavourable effect of the external medium.

Thus all the methods described for the formation of anisotropic coatings permit the achievement of any homogeneous tilted alignment of NLC.

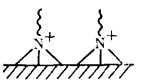
V. THE MECHANISMS OF THE ORIENTING EFFECT OF THE SURFACE

In the first studies undertaken to produce homogeneously aligned specimens it was already suggested that physicochemical forces play a decisive role in the mechanism of the alignment of NLC on a solid surface. On the basis of experimental observations, Friedel[20] concluded as early as 1922 that the NLC is aligned homeotropically on the support, provided that its molecules do not interact with the solid surface and in a planar manner in the presence of any kind of physicochemical interaction. The homogeneous alignment of NLC on supports rubbed with leather, paper, or fabric has been explained[177] by the dipole interaction of the liquid crystal molecules with the organic impurities transferred on to the surface during rubbing. The subsequent studies made it possible to refine these conclusions, but a complete understanding of the orienting effect of the support has not as yet been achieved. This is associated both with the inadequate theoretical development of the physical chemistry of surfaces and with the experimental difficulties due to the indefinite structure of the support and the lack of reliable methods for the measurement of the surface energy and the energy of the anchoring of the NLC to the support, the contamination of the liquid crystal material by decomposition products, and other causes.

Nematic liquid crystals usually consist of extended molecules ~20 Å long containing alkyl chains and alkoxy-, cyano-, azoxy-, and other polar groups and for this reason the intermolecular interaction with a solid surface can take place via both dispersion and polar forces (interactions of the dipole–dipole and dipole–induced dipole types) and hydrogen and other bonds. Account must also be taken of steric factors and, when a specific relief is created on the surface of the support, the anisotropic-elastic forces also play a significant role.

1. The Steric Model

Investigations of the intermolecular interaction of NLC with a solid surface have been stimulated by reports of the orienting influence of surfactants adsorbed on the support.[22–25] One of the first models[27,43] considered only steric factors on the assumption that surfactant molecules with long alkyl chains are arranged at right angles to the surface owing to the electrostatic interaction with the polar surface of the support, as happens for example, in the case of hexadecyltrimethylammonium bromide $C_{16}H_{33}N^+(CH_3)_3Br^-$ (HMAB):



Steric factors then favour the incorporation of the long NLC molecules parallel to the alkyl chains, i.e. the homeotropic alignment. Evidently this approach is important only in special cases.

2. The Criterion of Creagh and Kmetz

The first attempt at a thermodynamic explanation of the alignment of NLC on a solid surface was undertaken by Creagh and Kmetz,[15] who proposed that the difference between the surface energies of the support and the liquid crystal ($\gamma_S - \gamma_L$) be used as a measure of the free energy which determines the relative probability of the homeotropic alignment relative to the planar orientation. When $\gamma_S < \gamma_L$, the intermolecular forces within the NLC prove to be greater than the surface interaction forces, the liquid crystal does not wet the support and is aligned homeotropically. When $\gamma_S > \gamma_L$, the forces governing the anchoring to the surface predominate, the NLC wets the support, and is aligned in a planar manner.

The theoretical principles of this approach have been formulated by Porte.[33] If only dispersion forces operate between the NLC and the support, then the adhesion energy

W_a can be described by the Fowkes relation:[195]

$$W_a = 2(\gamma_L\gamma_S)^{1/2} \quad (2)$$

The equilibrium angle ϕ between the director and the normal to the surface corresponds to the condition for a minimum in the interfacial tension expressed in the form $\gamma_{SL}(\phi) = \phi_S + \gamma_L(\phi) - 2[\gamma_L(\phi)\gamma_S]^{1/2}$. The simplest calculation shows that the homeotropic alignment obtains when $\gamma_S < \gamma_L(0)$, the tilted alignment obtains when $\gamma_L(0) < \gamma_S < \gamma_L(\pi/2)$, and the planar alignment obtains when $\gamma_S > \gamma_L(\pi/2)$, which is consistent with the criterion of Creagh and Kmetz.

In view of the difficulty of the experimental determination of the surface energy of the support γ_S, it has been suggested that the critical surface energy γ_{cr} be used as the characteristic of the energy state of the orienting surface.[3]. The quantity γ_{cr} is found by extrapolating the results of measurement of the wetting angles θ for non-polar liquids with known values of $\gamma_L > \gamma_{cr}$ to $\theta = 0°$.[196] This empirical criterion has come to be widely used and was subsequently repeatedly tested.[28,42–45,76,197] However, the quantity γ_{cr} is not a fundamental property of the solid and depends on the nature of the liquids and the presence of adsorbed layers on the surface and the relative humidity. It has been shown that the critical surface energy is determined by the dispersion contribution to the surface energy of the support ($\gamma_{cr} = \gamma_S^d$) and can be used to characterise only non-polar surfaces.[198] The experimentally observed types of alignment are therefore by no means always consistent with the rule of Creagh and Kmetz.[7,28,42–45] Subsequent studies showed that this model constitutes only a special case of a more general mechanism of alignment.

3. The NLC–Support Polar Interaction

The polar interaction of NLC molecules with a charged solid surface is more difficult to describe theoretically than the dispersion interaction but it must be taken into account in considering the alignment mechanisms. The importance of allowing for polar forces has been demonstrated in a number of studies,[43–45] whose authors investigated systematically the alignment of MBBA on surfaces with different surface densities of adsorbed HMAB molecules. On a clean glass support, MBBA molecules are arranged parallel to the surface as a result of a dipole interaction. With increase in the density of the molecules of the orienting agent adsorbed on the glass the electrostatic field of the support is shielded. Finally, for the maximum density of HMAB molecules, only the dispersion component of the adhesion energy of MBBA remains and its molecules are oriented at right angles to the surface.

Thus, in describing the surface interaction of two phases with the aid of Eqn.(1), one must bear in mind that all the terms of this equation consist of dispersion and polar components: $W_a = W_a^d + W_a^p$; $\gamma_i = \gamma_i^d + \gamma_i^p$; $d_i + p_i = 1$, where $d_i = \gamma_i^d/\gamma_i$ and $p_i = \gamma_i^p/\gamma_i$ are the relative contributions of the dispersion and polar component of the surface energy, while i = L or S. The quantity γ_i^p can be made up in its turn of the following principal components: $\gamma_i^p = \gamma_i^{pp} + \gamma_i^{pi} + \gamma_i^h$, where γ_i^{pp} takes into account the dipole–dipole interaction, γ_i^{pi} the interaction of the dipole–induced dipole type, and γ_i^h the hydrogen and other bonds on the surface.

The total adhesion energy can be formulated as the sum of the dispersion component of the type defined by Eqn.(2) [$W_a^d = 2(\gamma_L^d\gamma_S^d)^{1/2}$] and the polar component, for which different expressions have been proposed. Thus Perez et al.[46] use an expression for W^p in terms of the electrostatic field of the support E: $W_a^p = E\delta\mu$, where δ is the number of NLC molecules per unit surface and μ the effective dipole moment of the NLC molecules, which depends on their alignment. Another expression for the total adhesion energy with allowance for polar factors has been proposed by Girifalco and Good:[199] $W_a = 2\Phi(\gamma_S\gamma_L)^{1/2}$, where Φ is the interaction parameter. When there are no polar forces, $\Phi = 1$ and this expression becomes identical with the Fowkes equation [Eqn.(2)] and the criterion of Creagh and Kmetz can be used to estimate the degree of alignment of the NLC on a solid surface. If the dipole–dipole interaction predominates among all types of polar interaction between the NLC molecules and the support, then the parameter Φ can be expressed in terms of the geometrical mean of the corresponding components of the surface energy:[200]

$$\Phi = (p_S p_L)^{1/2} + (d_S d_L)^{1/2}, \quad (3)$$

whereupon $W_a^p = 2(\gamma_S^p\gamma_L^p)^{1/2}$. It has been shown empirically that in many cases the harmonic approximation[46,200] can also be used to calculate W^p, which leads to the expression $W_a^p = 4\gamma_S^p\gamma_L^p/(\gamma_S^p + \gamma_L^p)$.

4. The Models of Alignment Based on the Girifalco–Good–Fowkes Equation

A whole series of studies[60,137,138,201–203] have considered models of the alignment of NLC on a solid surface employing the Girifalco–Good–Fowkes equation:[199] $\gamma_{SL} = \gamma_S + \gamma_L - 2\Phi(\gamma_L\gamma_S)^{1/2}$ or, after substituting Eqn.(3) for the parameter Φ:

$$\gamma_{SL}(\varphi) = \{[\gamma_L^d(\varphi)]^{1/2} - (\gamma_S^d)^{1/2}\}^2 + \{[\gamma_L^p(\varphi)]^{1/2} - (\gamma_S^p)^{1/2}\}^2. \quad (4)$$

Here the dependence of γ_L on the angle of alignment of the NLC ϕ is written in the form proposed by Parson:[204]

$$\gamma_L^d(\varphi) = \gamma_L^d(0) + \Delta\gamma_L^d \sin^2\varphi \ ;$$
$$\gamma_L^p(\varphi) = \gamma_L^p(0) + \Delta\gamma_L^p \sin^2(\varphi + \theta_p) \ . \quad (5)$$

The analogous relations for $\gamma_L(\phi)$ and $p_L(\phi)$ are also used.[201] Here $\Delta\gamma_L^{d,p} = \gamma_L^{d,p}(\pi/2) - \gamma_L^{d,p}(0)$ are the anisotropies of the dispersion and polar contributions to the surface energy of the NLC at the interface with a vacuum and the parameter θ_p takes into account the possible discrepancy between the directions of the dipole moment of the NLC molecules and the director.

The polar anchoring energy $W_\phi = \gamma_{SL}(\pi/2) - \gamma_{SL}(0)$, calculated by Eqns.(4) and (5) for MBBA [$\gamma_L^d(0) = 29$ mJ m^{-2}, $\gamma_L^p(0) = 9$ mJ m^{-2},[205] and $\Delta\gamma_L^d = \Delta\gamma_L^p = 4.5 \times 10^{-2}$ mJ m^{-2} [32]] on surfaces treated with organosilicon surfactants, is 20–54 mJ m^{-2},[138] which agrees with the measured values (Table 4). The experimental determination of the azimuthal anchoring energy $W_\alpha = \gamma_{SL}(\pi/2) - \gamma_{SL}(0)$ in terms of Eqn.(4) for heptylcyanobiphenyl on rubbed surfaces leads to values in the range 4×10^{-3}–5×10^{-2} mJ m^{-2}, while on SiO_x films sputtered at an angle $\psi = 30$ °C it leads to 8.8×10^{-2} mJ m^{-2} [206] (see Table 5 above).

The equilibrium angle ϕ can be calculated from the condition for a minimum in the interfacial energy: $\partial\gamma_{SL}/\partial\phi = 0$.

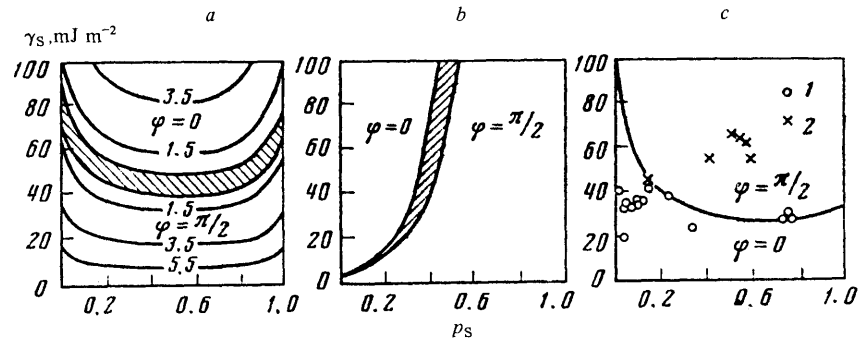


Figure 2. Alignment diagrams for the angle ϕ: *a*) for model NLC with the parameters $\gamma_L(\pi/2) = 40$ mJ m^{-2}, $\gamma_L(0) = 50$ mJ m^{-2}, $p_L(0) = p_L(\pi/2) = 0.5$; *b*) for MBBA according to Köhler's data:[201] $\gamma_L(\pi/2) = 29.1$ mJ m^{-2}. $\gamma_L(0) = 28.1$ mJ m^{-2}, $p_L(\pi/2) = 0.29$, $p_L(0) = 0.34$; c) for MBBA according to Naemura's data:[138] $\gamma_L^d(0) =$ 29 mJ m^{-2}, $\gamma_L^p(0) = 9$ mJ m^{-2}, $\Delta\gamma_L^d = \Delta\gamma_L^p = 0.045$ mJ m^{-2} [$\gamma_L(0) = \gamma_L(\pi/2) = 38$ mJ m^{-2}, $p_L(\pi/2) = p_L(0) = 0.24$]. The numerals opposite the curves indicate the values of W_ϕ (mJ m^{-2}); the transition region with $0 < \phi < \pi/2$ is shaded. Experimental points according to Naemura's data:[138] 1) for $\phi = 0$; 2) for $\phi = \pi/2$.

It has been suggested that the results of the calculation be represented in terms of the so-called alignment diagrams. where each point corresponds to a support with specific values of γ_S and p_S.[201] The alignment of the NLC molecules on such a surface is characterised by the position of this point relative to the boundary lines calculated by Eqns.(4) and (5) for $\phi = 0$ and $\phi = \pi/2$ (Fig.2*a*).

Table 5. Azimuthal energies of anchoring of NLC to various anisotropic surfaces.

Material of surface of support	Method of generation of surface anisotropy	Characteristics of surface relief		W_α, mJ m^{-2}		NLC	Refs.
		A, Å	λ, Å	calc.	expt.		
Glass	Rubbing	—	—	—	$7\cdot10^{-2}$	MBBA	[215]
ditto	ditto	—	—	—	$4\cdot10^{-2}$	CBP	[206]
SiO_2	»	—	—	—	$1\cdot10^{-2}$	CBP	[206]
PVA	»	—	—	—	$5\cdot10^{-2}$	CBP	[206]
Glass	Lapping with diamond paste	10	200	$8\cdot10^{-2}$*	—	—	[214]
ditto	Oblique sputtering of SiO_x	100	200	1.0*	$6\cdot10^{-1}$	MBBA	[140]
»	Ditto	—	—	—	$8.8\cdot10^{-2}$	MBBA	[206]
»	Diffraction gratings	250	3200	$1.2\cdot10^{-4}$*	—	—	[180]
»	Ditto	1700—2500	3300—8300	10^{-4}—10^{-5}*	—	—	[11]
»	Withdrawal from solution of $C_7H_{15}NH_2$	—	—	—	$5\cdot10^{-2}$	MBBA	[33]
»	Treatment with $(CH_3)_3SiCl$	—	—	—	$5\cdot10^{-3}$	MBBA	[216]
»	Without special treatment	—	—	—	$5\cdot10^{-3}$	MBBA	[217]
Quartz	Ditto	—	—	10^{-2}	—	CBP	[218]
ditto	»	—	—	$3\cdot10^{-2}$	—	PAA	[218]

*Calculation by Eqn.6.

The form of the alignment diagram depends on the parameters of the NLC: $\gamma_L^p(0)$, $\gamma_L^d(0)$, $\Delta\gamma_L^p$, and $\Delta\gamma_L^d$. Thus Figs.2*b* and 2*c* present the alignment diagrams for MBBA calculated from Köhler's results[201] and Naemura's results.[137] The significant difference between the accuracies of the predictions of the type of alignment can be accounted for by the difference between the accuracies of the estimates of the molecular parameters of MBBA and primarily the sign of $\Delta\gamma_L^p$. The experimental observations of the alignment of MBBA on various supports carried out by Naemura[137,138] agree best with the alignment diagram shown in Fig.2c.

The example described clearly demonstrates the difficulty of using alignment diagrams associated with the lack of reliable methods for the measurement of the components of the surface energies for both the NLC and the solid surface. Even the measurement of the surface energy of the NLC by familiar procedures, such as the Wilhemy plate, sessile drop, and capillary rise methods, leads to a scatter of the values of γ_L for the same material up to 30%. This can be caused both by the non-equilibrium conditions in the measurements and by the presence of impurities in the NLC. The values of γ_L for different NLC range from 25 to 40 mJ m^{-2}.[7,207–211]

The experimental determinations of the anisotropy of the surface tension $\Delta\gamma_L$ are available in the literature for only two NLC: 4.5×10^{-2} mJ m^{-2} for MBBA [32] and 5×10^{-3} mJ m^{-2} for cyanopentylbiphenyl.[134] It is noteworthy that such a low value of $\Delta\gamma_L$ corresponds to the virtual absence of a transitional region with $0 < \phi < \pi/2$ from the alignment diagram.

The determination of the surface energy of the solid surface presents even greater difficulties, since it cannot be measured directly. Furthermore, the structure of the surface of the support is as a rule undetermined and depends on the conditions of preparation, heat treatment, and purification of the supports. For example, the undetermined adsorption of the vapour of the liquid diminishes the interfacial free energy at the solid surface–vacuum interface by an amount $\gamma_{SG} = \gamma_S - \pi_0$. Owing to the lack of experimental data, the value of π_0 is usually neglected, by assuming it to be small compared with γ_S and γ_L. At the same time according to Adamson's data,[8] the ratio $\pi_0/\gamma_L = 0.1$–0.3 for polar liquids, so that the above assumption is not always correct.

Thus for a correct representation of the physicochemical interaction of NLC with solid surfaces, further experimental studies in this field are essential, because only they can demonstrate the practical value of the models described above.

5. The Alignment of NLC on Cleavage Surfaces of Single Crystals

This aspect of the interaction of NLC with a solid surface has so far been little investigated, although the first experiments on the alignment of *p*-azoxyanisole on fresh cleavage surfaces of NaCl crystals were carried out as early as the beginning of this century. It has been shown that the layer of NLC on the cleavage surface of a single crystal can be divided into separate regions, within which the director is aligned in certain cases along simple crystallographic directions: for example, this is the [110] or [1$\bar{1}$0] direction for the (001) face of the NaCl crystal.[9] In the general case the alignment of the director in the cleavage plane depends on the symmetry of the single crystal[212] and for ferroelectric materials it also depends on the direction of the spontaneous polarisation vector and on the dielectric anisotropy of the NLC.[213]

The study of the characteristics of the alignment of liquid crystals on the cleavage surfaces of single crystals of different structure should make an additional contribution to the understanding of the mechanism of the physicochemical interaction of NLC with a solid surface.

6. The Elastic Interaction of NLC with a Textured Surface

In order to account more fully for the orienting effect of the support, it is necessary to consider, apart from physicochemical forces, also anisotropic-elastic forces in the NLC layer. A simple explanation of the homogeneous alignment of NLC on surfaces having a relief in the form of parallel grooves has been proposed.[178,214] It is based on the calculation of the additional elastic energy ΔW which the NLC molecules would have had as a consequence of deformation near the textured surface if they had been oriented at right angles and not parallel to the grooves. In the absence of other orienting factors, ΔW is the azimuthal anchoring energy W_α. If the surface relief is described by a sinusoidal function with an amplitude A and a wavelength λ, then the above energy is defined by the following expression on the assumption of strong anchoring of the NLC to the support:

$$\Delta W = 2\pi^3 k A^2/\lambda^3 \qquad (6)$$

where k is the elastic constant of the NLC.

The anchoring energies W_α, calculated by Eqn.(6) for different anisotropic surfaces, are listed in Table 5. Evidently there is a satisfactory agreement between the calculated and experimental W_α and, owing to their finer texture, the films sputtered at an angle make it possible to obtain an anchoring energy higher by an order of magnitude than for rubbed surfaces.

The low tilt angle of NLC molecules on rubbed supports can apparently be accounted for by the asymmetric form of the grooves arising under the conditions of a non-uniform mechanical action.[151] The minimisation of the energy of elastic deformation on sputtered films leads to different tilt angles of the director as a function of the parameters of the surface relief of the films.[139,188]

According to the elastic mechanism of orientation, the azimuthal energy of the anchoring of the NLC to the support can be regulated by altering the amplitude and wavelength of the surface relief. However, competition between the anisotropic physicochemical forces and the anisotropic-elastic forces can prevent the alignment of the NLC molecules along the grooves. Thus when during the coating of the working cell the stream of the liquid crystal material is directed at right angles to the grooves, the direction of the director deviates from that of the grooves by an angle which increases with the width of the grooves and gives a smaller value of ΔW. The energy W_α of the anchoring of NLC to the surfaces of surfactant films having an ordered molecular structure is of the same order of magnitude as ΔW for rubbed surfaces (Table 5). In particular, as a result of this agreement, the rubbing of extended polymer films in a direction which does not coincide with that of the long molecular axis of the polymer leads to the breakdown of the orientation of the NLC.[93] The anisotropy of the surface energy of sputtered films[206,219] and films which have been rubbed on[206] also indicates the need to allow for the physicochemical properties of the support together with the geometry of its surface.

Thus the interfacial interaction of NLC with a solid surface determines characteristics such as the polar angle ϕ and the polar anchoring energy W_ϕ, while the direction of the director α and the azimuthal anchoring energy W_α are specified both by anisotropic-elastic forces, related to the geometry of the surface of the support, and by anisotropic physicochemical forces.

VI. EXAMPLES OF THE PREPARATION AND APPLICATIONS OF ALIGNED NEMATIC LIQUID CRYSTALS

In the technology of the preparation of liquid crystal displays, the selection of the method for orienting the NLC whereby the required tilt angle of the director can be achieved necessitates the allowance for factors such as the chemical structure of the NLC, the composition of the glass employed for the support, the technological intermediate layers, the dimensions of the support, and the temperature regime of the subsequent operations. The correct choice of the method of cleaning the surface plays a very important role. In order to eliminate the influence of alkali metal ions diffusing from the glass, it is desirable to employ a sublayer of an oxide or polymeric material. Certain examples of technological processes for the creation of various types of orientation are given below.

1. Homogeneous Alignment of NLC

Deposition of PVA Films with an Ordered Molecular Structure (by the Langmuir–Blodgett Method)

Glass plates with an electrode pattern are coated with silicon oxide, washed in an ultrasonic bath with a peroxide–ammonia mixture, washed with deionised water, and dried by centrifugation. A bath with a mobile barrier is filled with an aqueous PVA solution (0.03 wt.%) and cassettes with the plates are immersed in it. With the aid of the mobile barrier, an oriented monolayer of PVA molecules is established on the surface of water and the cassette is withdrawn from the solution, after which the plates are heat-treated at 150 °C for 20 min. The angle of tilt achieved is $\beta = 0° \pm 0.5°$ and the director is aligned at right angles to the direction of withdrawal. The orienting capacity of the films persists up to 160 °C.[191]

The Rubbing on of Polyimide Films

Glass plates with an electrode pattern are washed in hot chromic acid mixture and water and then treated with an aqueous solution of γ-aminopropyltriethoxysilane (0.1 wt.%) and dried by centrifugation. A solution of polypyromellitamidoacid in dimethyl formamide (5 wt.%) is deposited on the

plates by immersion with subsequent centrifugation at 3000 rev min^{-1}. The plates are maintained successively at 80°, 130°, and 300 °C, 30 min at each temperature. The polyimide film formed is rubbed with Kapron brushes; the tilt angle of the director achieved is $\beta \cong 1-3°$ and the director is aligned along the direction of rubbing. The orienting capacity of the film persists up to 450 °C.[95,103]

The Oblique Sputtering of Germanium Monoxide

A film of germanium monoxide 200–250 Å thick is sputtered onto glass plates by one of the technological procedures described with a temperature of the source of 800–850 °C, at a pressure of 5×10^{-3} Pa and at an angle $\psi = 30-50°$ relative to the surface of the support. The angle of tilt of the director achieved is $\beta = 0°$ and the director is perpendicular to the direction of the beam of the sputtered substance. The film retains its orienting capacity up to 450 °C.[145]

2. The Tilted Alignment

The Sputtering of Germa ium Mo oxide

The sputtering of GeO under the conditions described in the previous example at an angle of 5–8° relative to the surface of the support makes it possible to achieve a tilt angle of the director $\beta = 25-35°$.[145]

Double Oblique Sputtering of Silico Oxide

A second film ~10 Å thick is sputtered at an angle $\psi = 30°$, after rotating the support by 90° relative to the normal to the surface, on top of a film of silicon oxide 200–300 Å thick which had been sputtered at an angle of 5° relative to the surface of the support; the temperature of the source is 1300–1400 °C and the pressure is 10^{-2} Pa. The angle of tilt of the director achieved is $\beta = 0-30°$ and the orienting film withstands heating to 500 °C.[159]

Treatment of Sputtered Geo or Sio Films with a Solution of Lecithin

Plates treated by one of the methods described in previous examples are immersed in an alcoholic solution of lecithin (1 wt.%) and are then dried at 80 °C for 30 min. The angle of tilt β achieved increases to 60–90° and the azimuthal alignment is retained; the alignment does not change on heating to 200 °C.[7]

3. The Homeotropic Alignment of NLC

Deposition of Multilayers of α Cetylacrylic Acid by the Langmuir–Blodgett Method

Glass plates with an electrode pattern are washed in hot chromic acid mixture in water and are dried in a centrifuge. They are then immersed in a 60 × 15 × 8 cm^3 bath filled with deionised water on the surface of which 0.1 cm^3 of a 0.1% solution of α-cetylacrylic acid in heptane has been deposited. With the aid of a mobile barrier, an aligned monolayer of α-cetylacrylic acid is formed on the surface of water, whose surface tension then diminishes from 71 to 40 mJ m^{-2}. The plates are withdrawn from the bath, displacing the barrier so that the surface tension of water remains constant. They are then kept at 110 °C for 10 min. The orienting properties of the layer are retained up to 200 °C.[191]

Treatment of the Supports by Carboxylatochromium Complexes

Glass plates with an electrode pattern are washed as in the previous experiment and are then immersed in a solution of stearatochromium chloride [chromolin {Edoran in original—(Ed.of Translation)}] (0.1 wt.%) for 30–40 s, after which they are kept at 120 °C for 20 min. The orienting capacity of the layer is retained up to 400 °C.[50]

4. The Relation Between the Alignment Parameters and the Electro-optical Characteristics of the NLC

The choice of a particular type of alignment of NLC in liquid crystal displays is achieved depending on the electro-optical effect employed, the properties of the NLC, and the required parameters and design of the apparatus. Thus, in order to attain the *B*-effect, the "guest–host" effect (using dyes), and the cholesteric–nematic transition in thin layers, an initial homeotropic orientation is required. However, electro-optical effects involving the creation of an initial homogeneous alignment with $\beta = 0$, particularly with a twist structure for which the azimuthal directions of the director at the upper and lower supports form an angle which is usually close to $\pi/2$, are employed much more frequently.

The alignment parameters, especially the initial tilt angle of the director, exert a significant influence on the electro-optical characteristics of the NLC. Thus, with increase of the deviation from $\phi = 0$ or $\phi = \pi/2$, the threshold and controlling potentials diminish and the rapidity of the response improves; however, the contrast of the image and the steepness of the voltage–contrast characteristic are then somewhat impaired[142,220–221] and the range of angles of observation also diminishes considerably for displays based on the twist effect.[143] At the same time the use of a rigorously homogeneous or homeotropic alignment can lead to the appearance of various defects in the image caused by the equal probabilities of the rotation of the director in opposite directions under the influence of the electric field[148,149,222] and also by the curving of the potential field lines at the edges of the electrodes.[149,152] In preparing the displays, one therefore endeavours to achieve a small (by 1–5°) deviation of the director from $\phi = 0$ or $\phi = \pi/2$.

An interesting possibility for the attainment of optimum electro-optical characteristics has been demonstrated by the alignment effects under the conditions of a weak anchoring of the NLC to a solid surface.[133,223–225] A decrease of the anchoring energy W_ϕ promotes not only a decrease of the threshold potential and of the response time but also an increase of the steepness of the voltage–contrast characteristic, the overall effect of which makes it possible to increase the information capacity of the displays. For the twist effect, the realisation of this version is complicated by the additional requirement of a high anchoring energy W_α compared with the volume energy of twisting in order that the supports can maintain the twist deformation of the NLC.

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Thus intensive investigation of the orientation of NLC led to a diminution of the gap between theoretical studies in the physical chemistry of surfaces and the applied developments in the field of liquid crystal devices. The methods available at present make it possible to achieve a reliable specific alignment of NLC of various types. At the same time, a complete understanding of the mechanisms of the alignment process has not so far been achieved. In the immediate future questions concerning the interaction of NLC with a solid surface should apparently remain in the centre of attention of investigators. In particular, the study of electro-optical effects in NLC, under the conditions of their weak anchoring to the surface, in order to develop procedures for the attainment of the optimum characteristics of the indicator devices is of special interest.

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Conducting Compounds Based on Phthalocyanine Derivatives

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The methods of synthesis and the physicochemical properties of partly oxidised metallophthalocyanines and porphyrins are surveyed and described systematically. Special attention has been devoted to the electrical conductivities of these compounds and also to the analysis of the influence of various factors on the latter.
The bibliography includes 93 references.

CONTENTS

I. Introduction 144
II. Synthetic metals based on partly oxidised phthalocyanines 145
III. Synthetic metals based on partly oxidised porphyrins 146
IV. Film and polymeric conducting materials based on phthalocyanines 147

I. INTRODUCTION

The first organic metals, compounds in which electron transfer in the solid phase takes place via the organic component of the molecule, were first obtained in the 1960's. These substances are of considerable scientific and practical interest[1,2] and naturally a new field devoted to them, combining the methods of organic chemistry and solid state physics, has developed rapidly. The principal requirements which must be met in the specific synthesis of organic metals, the methods of their preparation, as well as their properties and structure have been examined in a number of investigations (see, for example, Refs.3–9).

The presence of the metallic state was first demonstrated rigorously for the quinolinium–TCNQ and *N*-methylphenazinium-TCNQ compounds, where TCNQ is tetracyanoquinodimethane.[10] The electrical conductivities σ of these complexes at room temperature are approximately $10^2\ \Omega^{-1}\ cm^{-1}$ and their temperature variation in the range 200–300 K is of the same character as for metals. A remarkable property of these complexes is an anomalously high dielectric constant.[11] Even higher values of σ, amounting to $2 \times 10^3\ \Omega^{-1}\ cm^{-1}$, have been observed in the tetrathiofulvalene–TCNQ[12] and (tetrathiotetracene)$_2$ I_3 [13] systems. In this case the metallic state is stable down to 40–60 K. It has been possible to stabilise the metallic state to the very lowest temperatures for the first time in the hexamethylenetetraselenofulvalene–TCNQ,[14] (tetraselenotetracene)$_2$Br, and (tetraselenotetracene)$_2$Cl [15–17] compounds. An important advance in this field has been the synthesis of organic superconducting systems: $(TMTSF)_2PF_6$, $(TMTSF)_2AsF_6$, and $(TMTSF)_2ClO_4$, where TMTSF is tetramethylenetetraselenofulvalene, and also bis(ethylenedithiolo)-tetrathiofulvalene iodides.[6,18–21] The conduction in all these compounds takes place in the organic component of the complexes. The organic component is also conducting in partly oxidised polymers with a system of covalent bonds.[5,22]

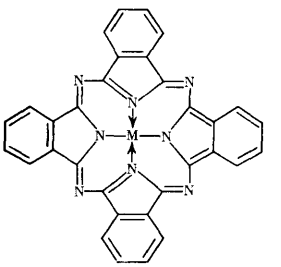
On the other hand, a class of partly oxidised inorganic complexes, exhibiting a conductivity of the metallic type [for example, $K_2Pt(CN)_4Br_{0.3}.3H_2O$] is known.[1] The molecules of these compounds have a square-planar structure and electron transfer in their specimens takes place via the metal–metal bond.

It has been found in recent years that conductivity of the metallic type obtains also in coordination compounds–partly oxidised phthalocyanines and their analogues. There are several possibilities for electron transfer in these substances: via the organic ligand with a branched system of conjugated bonds, via the complex-forming metal ion, and via the oxidant.

The aim of the present review is to survey the available data on the metal complex phthalocyanines and porphyrins exhibiting metallic properties and also to discuss the possibilities for further research in this field in order to obtain complexes with a high conductivity.

The electrical properties of phthalocyanines began to be investigated a fairly long time ago. In 1947 Eley and Vartanyan found independently that metal derivatives of phthalocyanines are semiconductors.[23] Extensive studies on the physicochemical properties of these macrocyclic compounds were then initiated. Interesting data in this field have already been obtained at the present time, particularly as regards the dark conductivity and photoconductivity of phthalocyanines and the influence on the latter of various chemical and physical factors.[24–29] The dependence of the conductivity on the temperature and pressure[22,30] and the role of the metal and of the adsorption of oxygen[31–37] and other gases[28,36] have been investigated and the infrared, ultraviolet, and EPR spectra of phthalocyanines have been examined; many of them have been studied by X-ray diffraction;[23,24,27,38–44] the electronic structure of phthalocyanines and the mechanism of the conduction in the latter have been discussed.[23,24,28,44–46] Phthalocyanines have been proposed as promising photoconductors for use in photocells with a blocking layer, as sensitisers for inorganic semiconductors, and as thin-film electrodes.[45,47]

The synthesis of phthalocyanines with metallic and not semiconducting properties has arisen as a new stage; this was achieved by synthesising partly oxidised phthalocyanines and their analogues.[48–50]



metallophthalocyanine

Partial oxidation of various phthalocyanines and porphyrins leads to a new class of highly conducting organic compounds. A characteristic feature of their crystal structure is the presence of regular stacks consisting of electron donors and

acceptors. The distances between the molecules in the stacks comprising the donors are significantly smaller than the van der Waals distances and considerably smaller than the distances between the stacks themselves. As a result, the conducting electron system in such compounds is quasi-one-dimensional. The electrical conductivity is markedly anisotropic; it is a maximum along the long axis of the crystal and is smaller by several orders of magnitude in the transverse direction.

The salts $NO(BF_4)$ and $NO(PF_6)$,[51] tetracyanoquinodimethane,[52] chloranil, bromanil, and molecular bromine and iodine[53-59] have been used as reagents for the partial oxidation of phthalocyanines and porphyrins. Elemental iodine proved to be the most suitable oxidant; the reason for this selectivity is that iodine forms a large number of reduced species (I^-, I_3^-, I_5^-), which enables the donor systems to acquire the most favourable degree of partial oxidation. In addition, all three forms of reduced iodine are comparatively easy to identify by Raman spectroscopy.[60,61]

Metallophthalocyanines (MPc) and metalloporphyrins are oxidised under identical conditions. The reactions are reversible and the equilibrium is displaced towards the starting materials on heating the dry product *in vacuo*.[62]

$$MPc + (x/2)\,I_2 \rightleftharpoons MPcI_x$$

M = Fe, Co, Ni, Cu, Pt, H_2, Al, Ga, Ge, Sn, Si, Pb, REE

(lanthanide elements)

Table 1. The conductivities of pressed polycrystalline $MPcI_x$ specimens at 300 K.[49,53,62]

Compound	x	σ, Ω^{-1} cm^{-1}	E_a, eV
$CuPcI_x$	1.71	4.2	0.0121
$PtPcI_x$	0.93	2.4	0.016
H_2PcI_x	2.2	2.3	0.040
$NiPcI_x$	0.00	$1\cdot10^{-11}$	1.6
$NiPcI_x$	0.56	0.7	0.024
$NiPcI_x$	0.58	2.2	—
$NiPcI_x$	1.00	0.7	0.036
$NiPcI_x$	1.07	7.7	—
$NiPcI_x$	1.44	7.7	—
$NiPcI_x$	1.68	0.8	0.021
$NiPcI_x$	3.81	0.6	—
$CoPcI_x$	0.00	$2\cdot10^{-10}$	1.6
$CoPcI_x$	0.60	0.1	0.065
$CoPcI_x$	1.00	0.06	0.082
$FePcI_x$	0.00	$2\cdot10^{-10}$	—
$FePcI_x$	1.93	$4\cdot10^{-3}$	0.127
$FePcI_x$	2.74	$2\cdot10^{-3}$	0.070
$FePcI_x$	3.85	$1\cdot10^{-4}$	0.254
H_2Pc-chloroanil	—	10^{-2}	—

II. SYNTHETIC METALS BASED ON PARTLY OXIDISED PHTHALOCYANINES

Methods of synthesis of polycrystalline and single crystal specimens of partly oxidised phthalocyanines have now been developed. In order to obtain the polycrystalline forms, powdered metallophthalocyanines are mixed with iodine in chlorobenzene; iodinated phthalocyanines are collected by centrifugation, washed with hexane, and dried in an inert atmosphere. The products are black polycrystalline substances with different stoichiometries; the conditions of synthesis have been described.[62]

$NiPcI_{1.0}$ single crystals are grown in an H-shaped tube by the diffusion method from solutions of NiPc and iodine either in 1,2,4-trichlorobenzene or in 1-chloronaphthalene.[50] The iodination of NiPc single crystals does not lead to $NiPcI_x$ single crystals, since the formation of a complex entails the impairment of the structure and decomposition of the crystal. The Raman spectra of $NiPcI_x$ exhibited an intense absorption at 107 cm^{-1}, which is characteristic of the polyiodide I_3^-. Bands due to I_2 or I_5^- (212 and 167 cm^{-1} respectively) were not detected in the spectra, which indicates the absence of these forms from the products.[49,50,60] This finding has also been confirmed by ^{129}I Mössbauer spectroscopy.[49]

The results of measurements of the conductivities of the polycrystalline specimens are presented in Table 1. Such conductivities include effects due to intraspecies contact resistance, but they are nevertheless comparable with those of other organic metals. It is noteworthy that the single crystal conductivities of the organic metals obtained at the present time usually exceed the conductivities of the powder by a factor of 10^2–10^3. In view of this, the data in Table 1 show that the phthalocyanines are promising electron donors for the formation of highly conducting organic molecular crystals.

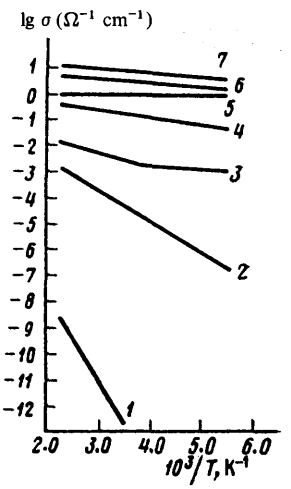


Figure 1. Variation of the electrical conductivities of pressed polycrystalline specimens with $1/T$: 1) CuPc; 2) $FePcI_{3.85}$; 3) $FePcI_{2.7}$; 4) $CoPcI_{0.6}$; 5) $NiPcI_{0.59}$; 6) $PtPcI_{0.93}$.

The temperature variation of the electrical conductivities of the pressed polycrystalline specimens is illustrated in Fig.1, which shows for comparison also the variation of the conductivity of unoxidised polycrystalline copper-phthalocyanine.

The interaction of iodine with $PcLnPc_{ox}$, where Pc_{ox} is the oxidised phthalocyanine ligand and Ln represents tervalent lanthanide elements such as Lu, Y, La, etc., has been investigated. The addition of iodine leads to a sharp increase of the electrical conductivity of the powder. Thus, for Ln = Pr, Sm, or Eu, the conductivities of the pressed specimens of the iodine complexes are higher by one order of magnitude relative to the unoxidised specimens and, in the case where Ln = Tb, Er, Tm, or Lu, the conductivity is higher by 3–4

orders of magnitude.[63,64] Iodinated complexes of di(phthalocyaninato)neodymium(III), i.e. $H[Nd^{III}(Pc)_2I_x]$, exhibit a high conductivity. When $x = 1,3$, the conductivity of the pressed polycrystalline specimen at room temperature is $6.4 \times 10^{-2}\ \Omega^{-1}\ cm^{-1}$, whereas for $x = 1.8$ it amounts to $8 \times 10^{-1}\ \Omega^{-1}\ cm^{-1}$.[65] On the basis of these results, the authors[63,64] suggested that iodide ions penetrate into the crystal lattice and form charge-transfer complexes having added to the nitrogen mesoatom of the macroring of the phthalocyanine ligand.

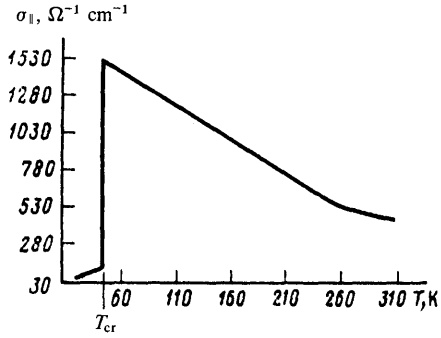


Figure 2. Temperature variation of the electrical conductivity of $NiPcI_{1.0}$ single crystals.[62]

Data on electrochemical transformations and on the conductivity of the products have been reported in the literature.[66,67]

Fig. 2 illustrates the temperature dependence of the electrical conductivity of $NiPcI_{1.0}$ single crystals in the direction of the stacks. At room temperature the conductivity of 65 specimens varied in the range 260–750 $\Omega^{-1}\ cm^{-1}$, the mean amounting to 550 $\Omega^{-1}\ cm^{-1}$. The temperature T_{cr} varies only slightly for different crystals and usually amounts to 90–100 K, although it reaches 52 K for some specimens.[62] When the specimen is cooled to a temperature below T_{cr}, the conductivity falls sharply. Such behaviour is comparable to that of the temperature dependence of the conductivity of the tetrathiofulvalene–TCNQ organic metal and shows that there is a Peierls transition or a first-order transition. The Raman spectra of the specimens show that in this transition the average degree of oxidation of NiPc remains unchanged down to 4 K.[62] The conductivity of the crystals cooled to a temperature below T_{cr} does not return to the initial value when they are reheated to the initial room temperature. On repeated cooling of the specimens, the Peierls transition takes place at a higher temperature T_{cr}.[62]

Later investigations showed that microcracks appear in the $NiPcI_{1.0}$ crystals on cooling. The sharp decrease of conductivity, which has been attributed to the Peierls transition, is in fact associated precisely with this phenomenon. When $NiPcI_{1.0}$ crystals, mounted without mechanical stresses on thin silvered graphite filaments, are cooled, the conductivity increases to a maximum value of $5 \times 10^3\ \Omega^{-1}\ cm^{-1}$ at 25 K (Fig. 3). On further cooling, the conductivity gradually falls, but its value does not tend to zero even at 0.1 K, in contrast to other molecular crystals.[68]

Whereas both in conducting complexes of this kind and in the Krogmann salt $[K_2Pt(CN)_4Br_{0.3}.3H_2O]$[69] the transport properties may be almost fully attributed to the metal while the ligands play only an indirect role in the electron transfer, in organic metals of the phthalocyanine series the ligands are actually responsible for conduction. The metal ion in such a complex modifies markedly the properties of the ligand but is not involved directly in the transport process itself.[49,60] In the synthesis of a conducting complex the ligand and not the metal is oxidised; electron transport takes place mainly via the highly conjugated π-electron clouds of the ligand. The delocalisation of the charge carriers along the stack of phthalocyanine molecules is indicated by the appearance in the EPR spectrum of a band, narrowed by the exchange interaction between the ligand π orbitals, with a g-factor of 2.032, i.e. close to the g-factor for the free electron.[70,71]

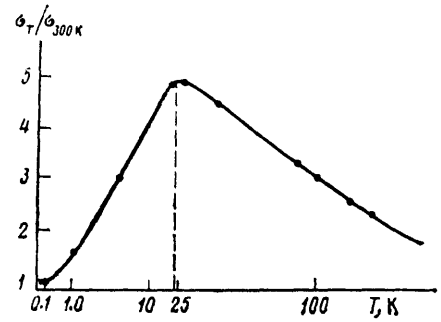


Figure 3. Temperature variation of the electrical conductivity of $NiPcI_{1.0}$ single crystals.[68]

The cross-sectional area of the phthalocyanine molecule is 2.5 times greater than that of the conducting stacks of known organic metals.[49] It is therefore of interest to compare the properties of individual charge carriers in $NiPcI_x$ and other conducting compounds obtained within the framework of the one-electron band theory of activity. According to this theory, the conductivity is related to the free path length λ and to the cross-sectional area of the conducting stack a by the equation[50,62]

$$\sigma = 2e^2\lambda/\pi\hbar a$$

where e is the electronic charge. For $NiPcI_{1.0}$ at room temperature, λ = 3.3–8.2 Å, which is equivalent to 1.0–2.3 intermolecular distances. These values are comparable to those for other highly conducting quasi-one-dimensional systems; 2.1–2.8 intermolecular distances for (tetrathiotetracene)$_2I_3$; 1.6–2.5 for hexamethylenetetraselenofulvalene–TCNQ; 0.4–0.6 for tetrathiofulvalene–TCNQ; 0.6 for $K_2Pt.(CN)_4Br_{0.3}.3H_2O$; 0.15 for quinoline–$(TCNQ)_2$.[62] Hence one may conclude that the large cross-sectional area of the $NiPcI_{1.0}$ molecules is not the cause restricting the attainment of a conductivity higher than the value obtained.

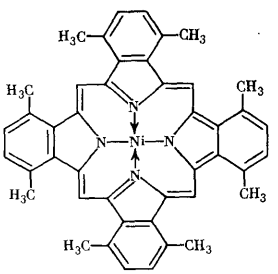
In conclusion one must note that at present there are no literature data for the influence of the crystalline modification of phthalocyanines on the electrical conductivities of their partially oxidised forms, although they would be of considerable theoretical and practical value.

III. SYNTHETIC METALS BASED ON PARTLY OXIDISED PORPHYRINS

The study of organic metals based on porphyrins is of great interest, since their structural wide variety permits a whole series of important conclusions and generalisations. Here we

shall discuss synthetic metals based on nickel 1,4,5,8,9,12, 13,16-octamethyltetrabenzoporphyrinate Ni(OMTBP), nickel tetrabenzoporphyrinate Ni(TBP), metallo-octaethylporphyrins M(OEP), and nickel tetramethylporphyrinate Ni(TMP).

The oxidation of Ni(OMTBP) with iodine in 1,2,4-trichlorobenzene yields, in particular, dark red $Ni(OMTBP)I_{1.08}$ crystals. Oxidation with iodine in chlorobenzene results in the formation, apart from the above crystals, of bronze needles having the composition $Ni(OMTBP)I_{2.0}$. The stoichiometric ratio of these complexes apparently depends on the solvent and the crystal growth conditions, but $Ni(OMTBP)I_{1.08}$ crystals almost always predominate.[60,72,73] The mixture of crystals is separated by physical methods on the basis of the colour and shape of the crystals.



Nickel 1,4,5,8,9,12,13,16-octamethyltetrabenzoporphyrinate

The Raman spectra of these compounds contain bands corresponding to the resonance absorption by the polyiodide I_3^-.[50] The degree of oxidation is 0.36 for $Ni(OMTBP)I_{1.08}$ and 0.97 for $Ni(OMTBP)I_{2.9}$.

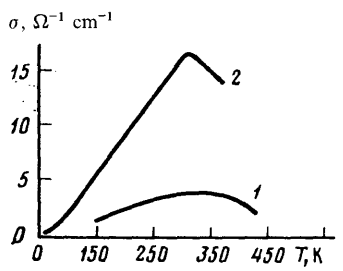
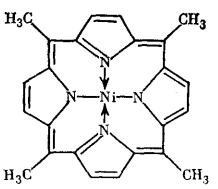


Figure 4. Temperature variation of the electrical conductivity of $Ni(OMTBP)I_x$ single crystals.[50]

The temperature variation of the conductivity in the direction of the stacks is illustrated in Fig. 4 for $Ni(OMTBP)(I_3)_{0.36}$ and $Ni(OMTBP)(I_3)_{0.97}$. On decrease of temperature below 350 K, the conductivity of the complex $Ni(OMTBP)(I_3)_{0.36}$ resembles that of metals. It increases slowly, reaching a maximum at 300 K; when the specimen is cooled, the conductivity diminishes. The temperature variations of the conductivities of $Ni(OMTBP)(I_3)_{0.97}$ and $Ni(OMTBP)(I_3)_{0.36}$ are analogous. Thus a change in the degree of partial oxidation for the Ni(OMTBP) systems leads only to a quantitative alteration of the function $\sigma(T)$ without changing at the same time its qualitative character.[50] The values of σ at room temperature and the shapes of the $\sigma(T)$ curves for $NiPcI_{1.0}$ and $Ni(OMTBP)I_x$ differ markedly from one another, which shows that slight structural changes in the macroring can alter significantly the properties of the organic metal.

Both compounds having the composition $Ni(OMTBP)I_x$ are, as shown above, conducting materials whose crystals are made up of stacks of partly oxidised macrorings in which electron transport is ensured by the ligands. The EPR spectra of the single crystals at different temperature have a line with a g-factor of 2.012.[62] This value is comparable with the analogous parameter for radicals and demonstrates the delocalisation of π electrons in the direction of the ligand stacks. $\lambda = 0.C6$ of the intermolecular distance has been obtained for $Ni(OMTBP)(I_3)_{0.36}$; magnetic susceptibility data and the results of X-ray diffraction analysis have been discussed in two investigations.[50,60] Since only very small crystals of $Ni(OMTBP)(I_3)_{0.97}$ are at present available, it has not been possible to carry out crystallographic studies on this substance.

Diffusion oxidation of Ni(TMP) with iodine leads to acicular $Ni(TMP)I_{1.0}$ crystals.[74] This substance is stable up to 70 °C, losing iodine at a higher temperature. It has been established by Raman spectroscopy that the degree of oxidation of $Ni(TMP)I_{1.0}$ is 0.33.



nickel tetramethylporphyrinate

The iodine chains in the $Ni(TMP)I_{1.0}$ crystals are arranged parallel to the axes of the porphyrin stacks and are located within the channels formed by the methyl and pyrrole hydrogen atoms. The EPR spectrum consists of a narrow anisotropic signal with $g = 2.0067$. The narrow line in the spectrum indicates the oxidation of the ligand:

$$Ni(TMP)I_{1.0} = [Ni(TMP)]^+ + [Ni(TMP)]_2(I_3)^- .$$

The free path length for $Ni(TMP)I_{1.0}$ is equal to 0.5 of the intermolecular distance.[74]

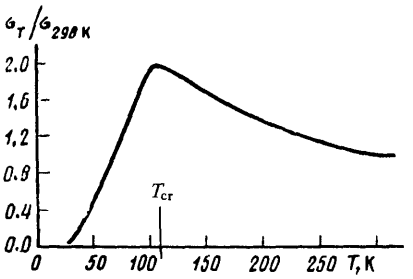


Figure 5. Temperature variation of the electrical conductivity of $Ni(TMP)I_{1.0}$ single crystals.[74]

The temperature dependence of the conductivity of the $Ni(TMP)I_{1.0}$ crystals is illustrated in Fig. 5. The plot shows that, with decrease of temperature from room temperature to $T_{cr} = 110$ K, the conductivity acquires a metallic character; on further reduction of temperature, the conductivity

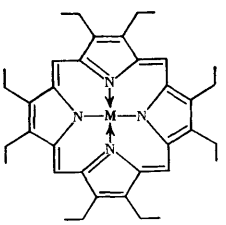
becomes thermally activated. On reheating and recooling of the specimen, hysteresis is not observed.[74]

Apart from the $Ni(TMP)I_{1.0}$ crystals, yet another complex of tetramethylporphyrin has been described, namely Ni(TMP)–TCNQ. Its crystals are made up of alternating donor and acceptor stacks. It has been observed that the infrared spectrum of the complex consists of a superposition of the spectra of the individual compounds. The conductivity of the Ni(TMP)–TCNQ crystals in the direction of their long axis has not been established accurately. It is only known that it does not exceed 10^{-5} Ω^{-1} cm^{-1} at room temperature.[75]

Table 2. The conductivities of polycrystalline $M(OEP)I_x$ specimens at 300 K.[76]

x	σ, Ω^{-1} cm^{-1}	E_a, eV
	$H_2(OEP)I_x$	
5.8	$3\cdot10^{-7}$	—
3.3	$2\cdot10^{-7}$	0.51
3.0	$1\cdot10^{-7}$	—
2.1	$2\cdot10^{-8}$	—
1.1	$1\cdot10^{-8}$	—
	$Cu(OEP)I_x$	
3.5	$6\cdot10^{-3}$	0.16
2.9	$4\cdot10^{-3}$	—
1.3	$4.4\cdot10^{-3}$	0.13
1.2	$3\cdot10^{-3}$	—
0.5	$2\cdot10^{-7}$	—
	$Ni(OEP)I_x$	
5.7	$2.8\cdot10^{-2}$	0.08
3.8	$1.8\cdot10^{-2}$	0.09
1.7	$2.8\cdot10^{-2}$	0.11
1.4	$1.4\cdot10^{-2}$	0.12
1.2	$6\cdot10^{-3}$	0.19
0.4	$1.5\cdot10^{-4}$	0.18

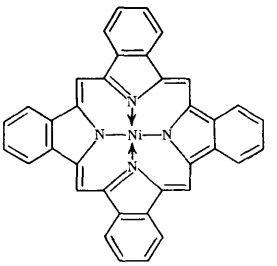
The products of the partial oxidation of metallo-octaethylporphyrins having the composition M(OEP), where M = Ni, Cu, or H_2, are of considerable interest.



metallo-octaethylporphyrin

They are important because the macroring (OEP) has a much less strained structure than in Pc and TBP. The complexes $M(OEP)I_x$ have been obtained by two procedures: the first by heating the complex M(OEP) with a (2–8)-fold excess of iodine for 24 h in an evacuated sealed tube and the second by mixing cooled solutions of M(OEP) and I_2 in chloroform; the product is obtained in the form of bright red single crystals.[76] The Raman spectra demonstrated the presence of iodine in the form of I_5^- (band at 167 cm^{-1}); consequently the degree of oxidation is $\rho = x/5$. The conductivity data for pressed polycrystalline $M(OEP)I_x$ specimens are presented in Table 2. In the course of the partial oxidation of M(OEP) an electron can be removed either from the *d* orbital of the metal or from the π orbital of the porphyrin ligand. ERP data have shown that the preferential oxidation of the ligand takes place,[76] which apparently means that the metals (Ni and Cu) do not play the main role in the conduction process.

A striking example of the fact that insignificant chemical transformations in the molecule entail a significant change in the physical properties of the synthetic metals is provided by the complex $Ni(TBP)I_{1.0}$, which differs from $Ni(OMTBP)I_{1.08}$ by the absence of eight methyl substituents and from $NiPcI_{1.0}$ by the replacement of the nitrogen mesoatoms by methylidyne groups.



nickel tetrabenzoporphyrinate

Raman spectra revealed the presence of an absorption at 107 cm^{-1}, which corresponds to I_3^- and the absence of the bands at 212 and 167 cm^{-1} characteristic of I_2 and I_5^- respectively. Thus the degree of oxidation is $\rho = 0.33$. The temperature dependence of the conductivity of $Ni(TBP)(I_3)_{0.33}$ single crystals is illustrated in Fig. 6. The compounds exhibit metallic properties in the temperature range from 300 to 95 K with a conductivity maximum of 600 Ω^{-1} cm^{-1}. On decrease of temperature below 95 K, $Ni(TBP)I_{1.0}$ becomes a semiconductor. Measurements of the conductivity of 200 $Ni(TBP)I_{1.0}$ single crystals at room temperature showed that $\sigma = 150–330$ Ω^{-1} cm^{-1}.[77] The free path length for $Ni(TBP)\cdot I_{1.0}$ single crystals is 2.1–4.3 Å or 0.66–1.3 intermolecular distances; for comparison, we may note that $\lambda = 60$ Å or 24 intermolecular distances for metallic nickel.[77]

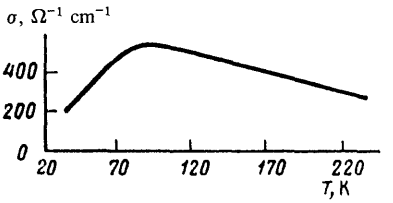


Figure 6. Temperature variation of the electrical conductivity of $Ni(TBP)I_{1.0}$ single crystals.[77]

In contrast to $Ni(OMTBP)I_{1.08}$ and $NiPcI_{1.0}$, in which charge transfer is associated with the delocalised π orbitals of the macroring, $Ni(TBP)I_{1.0}$ is a partly oxidised complex in which charge transport takes place via both the ligands and the complex-forming metal ions. The $[Ni^{II}(TBP)^+]$ cation can undergo electronic tautomerism, being converted thereby into $[Ni^{III}(TBP)]$. Thus the complex $Ni(TBP)I_{1.0}$ is a "connecting link" between purely organic and inorganic conducting coordination compounds. This is confirmed by EPR data. For the majority of the iodinated metalloporphyrins,

the g-factor is independent of temperature and is approximately equal to that for the free electron; the EPR signal is narrow and its width is also independent of temperature, which shows that the charge transfer in $NiPcI_{1.0}$, Ni(OMTBP)$.I_x$, and Ni(TMP)$I_{1.0}$ takes place via the ligand. In contrast to this, the g-factor and ΔH for Ni(TBP)$I_{1.0}$ are greater at room temperature and depend markedly on temperature.[78]

IV. FILM AND POLYMERIC CONDUCTING MATERIALS BASED ON PHTHALOCYANINES

The deposition of films of conducting dyes such as phthalocyanines can alter significantly the electronic-optical properties of various materials. Thus the metal-free phthalocyanine is used to sensitise amorphous selenium in xerography and silicon dioxide in the preparation of phototransistors. The efficiency of the operation of solar batteries can be increased by depositing a film of phthalocyanine or porphyrin. The only factor which limits at the present time the employment of these films is their low intrinsic conductivity.[79,80] Oxidation with iodine increases appreciably the conductivity of the film.[79] Fig.7 illustrates the temperature dependence of the conductivity of an $NiPcI_x$ film. Evidently, both after cooling and heating from room temperature, the $NiPcI_x$ film becomes more of an insulator. The decrease of conductivity on heating can be accounted for by the diffusion of iodine; the cause of its decrease on cooling is so far obscure. These data are inconsistent with the temperature variation of the conductivities of analogous complexes measured by Martinsen et al.[68] Iodination of thin PcCo, PcCu, and PcPb films increases their conductivity to 10^{-3}–10^{-1} Ω^{-1} cm^{-1}.[81]

The polymerisation of $M(OH)_2Pc$, where M = Si, Ge, or Sn, at 300–400 °C in a high vacuum (10^{-3} mmHg) (Fig.8) leads to the corresponding phthalocyaninato-polysiloxanes and the corresponding polygermoxanes, and polystannoxanes in satisfactory yields.[82,83] The polymers are stable in air; iodine can be removed by heating *in vacuo* above 100 °C. The degrees of polymerisation are $n_{SiPc} \geq 120$, $n_{GePc} \geq 60$, and $n_{SnPc} \geq 115$. Raman spectroscopy demonstrated the presence of the alloying component in the form of I_3^- together with a small amount of I_5^-. The conductivities of the $\{[M(Pc)O]I_x\}$ polymers vary in the sequence $\sigma_{Si} > \sigma_{Ge} > \sigma_{Sn}$, which is apparently associated with increasing interplanar distances, amounting to 3.33 Å for Si–O–Si, 3.51 Å for Ge–O–Ge, and 3.95 Å for Sn–O–Sn.

The conductivities of the specimens obtained depend on the concentration of the alloying component (Fig.9) and temperature.[82,84] The conductivities of the $\{[M(Pc)O]I_x\}$ polycrystalline species at 300 K are listed in Table 3; they are comparable to the analogous parameters for $MPcI_x$, M(OMTBP)I_x, and M(TBP)I_x.

Figure 7. Temperature variation of the electrical conductivity of an $NiPcI_x$ film.[77]

The EPR spectra show that the partial oxidation involves the ligand orbitals without affecting the metal atom.[84] It is known that the single crystal conductivity of quasi-one-dimensional materials in the direction of molecular stacks is usually 10^2–10^3 times greater than the conductivity of polycrystalline specimens. It is therefore possible that the complexes $\{[M(Pc)O].I_x\}_n$, where M = Si or Ge, have metallic properties in the form of single crystals.

Partial oxidation of the quasi-one-dimensional complexes $[Al(Pc)F]_n$ and $[Ga(Pc)F]_n$ with iodine ensures a high conductivity (0.01–0.1 Ω^{-1} cm^{-1}). The iodination of $[M(Pc)F]_n$ was carried out at room temperature, or by keeping $[M(Pc)F]_n$

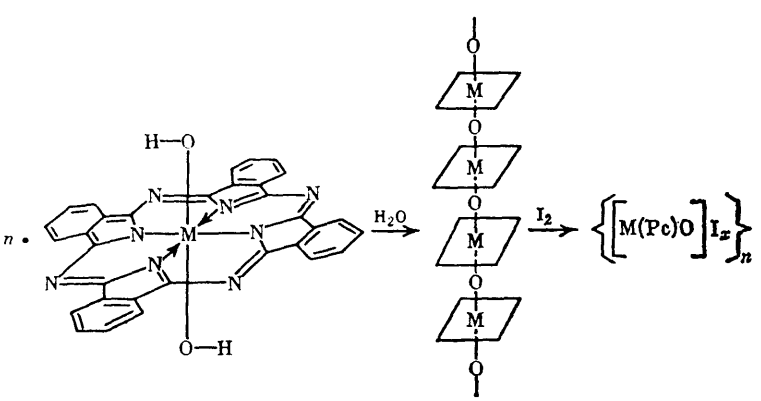


Figure 8. Schematic illustration of the preparation of $\{[M(Pc)O]I_x\}_n$.

in I_2 vapour for 7–21 days until the attainment of constant weight, or by stirring a suspension of $[M(Pc)F]_n$ in a solution of I_2 in hexane for 24 h. Raman spectroscopy demonstrates the presence of I_3^- (the band at 106–108 cm^{-1}) and the absence of I_2 and I_5^-.[85,86] The conductivities of the specimens obtained were measured on discs at 295 K (Table 4).

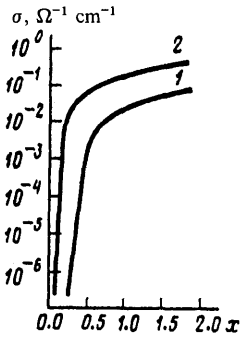


Figure 9. Dependence of the electrical conductivity of $\{[M(Pc)O]I_x\}_n$ on the iodine concentration: 1) M = Si; 2) M = Ge.[84]

Table 3. The electrical conductivities of polycrystalline $\{[M(Pc)O]I_x\}_n$ specimens at 300 K.[84]

Compound	σ, Ω⁻¹ cm⁻¹	E_a, eV
$[Si(Pc)O]_n$	$3\cdot10^{-8}$	—
$\{[Si(Pc)O]I_{0.5}\}_n$	$2\cdot10^{-2}$	—
$\{[Si(Pc)O]I_{1.4}\}_n$	$2\cdot10^{-1}$	0.04
$\{[Si(Pc)O]I_{4.6}\}_n$	$1\cdot10^{-2}$	—
$\{[Si(Pc)O]Br_{1.0}\}_n$	$6\cdot10^{-2}$	—
$\{[Ge(Pc)O]_n$	$<10^{-8}$	—
$\{[Ge(Pc)O]I_{1.8}\}_n$	$3\cdot10^{-2}$	0.08
$\{[Ge(Pc)O]I_{1.9}\}_n$	$5\cdot10^{-2}$	0.06
$\{[Ge(Pc)O]I_{1.94}\}_n$	$6\cdot10^{-2}$	0.05
$\{[Ge(Pc)O]I_{2.0}\}_n$	$1\cdot10^{-1}$	—
$\{[Sn(Pc)O]\}_n$	$<10^{-8}$	—
$\{[Sn(Pc)O]I_{1.9}\}_n$	$1\cdot10^{-6}$	—
$\{[Sn(Pc)O]I_{5.5}\}_n$	$2\cdot10^{-4}$	0.68

The conductivities of $\{[Al(Pc)F]I_x\}_n$ are higher than those of the gallium derivatives for high values of x, which is correlated with the greater interplanar spacings in the Ga polymer compared with the Al derivative and constitutes apparently yet another piece of evidence showing that the conductivity is ensured by the inter-ring overlap of the π orbitals. The highest conductivity obtained is 5 Ω^{-1} cm^{-1} for $\{[Al(Pc)F]I_{3.3}\}_n$; the conductivity of $\{[M(Pc)F]I_x\}_n$ is equal to or even greater than that of the SiO analogues. It is believed,[85,86] that this can be accounted for by the higher purity of $[M(Pc)F]_n$ compared with $[Si(Pc)O]_n$.

A characteristic feature of the structure of $\{[Ga(Pc)F]I_x\}_n$ is that the phthalocyanine rings cover one another, while in other structures they are displaced by an angle of 40° and above (Fig. 10). For this arrangement of the ligands in the stack of $\{[Ga(Pc)F]I_x\}_n$ molecules, a greater degree of overlap of the π orbitals between them should be ensured. This is apparently the explanation of the conductivity of 0.12 Ω^{-1} cm^{-1} of pelleted $\{[Ga(Pc)F]I_{0.93}\}_n$, which is extremely high even when account is taken of the interplanar distance (3.86 Å). For comparison, we may note that the conductivity of $NiPcI_{1.0}$ is 0.7 $\Omega^{-1}cm^{-1}$ for a distance between the molecules of 3.24 Å.[87]

Table 4. The electrical conductivities of polycrystalline $\{[Al(Pc)F]I_x\}_n$ and $\{[Ga(Pc)F]I_x\}_n$ specimens at 295 K.[85,86]

I/Al	σ, Ω⁻¹ cm⁻¹	I/Ga	σ, Ω⁻¹ cm⁻¹
0.00	$1.5\cdot10^{-4}$	0.00	10^{-6}
0.21	$1.8\cdot10^{-2}$	0.17	$1.9\cdot10^{-4}$
0.29	$1.5\cdot10^{-2}$	0.62	$1.7\cdot10^{-2}$
0.38	$2.0\cdot10^{-2}$	0.77	$4.4\cdot10^{-2}$
0.87	0.70	0.97	$7.2\cdot10^{-2}$
1.0	0.13	0.98	$8.6\cdot10^{-2}$
1.5	0.19	2.3	0.15
2.4	0.63	—	—
3.3	5.0	—	—

Among the partly oxidised quasi-one-dimensional complexes Al(Pc)Y and Ga(Pc)Y, where Y = F, Cl, or OH, we may note materials doped with $[BF_4]^-$, $[PF_6]^-$, and $[SbF_6]^-$. Owing to the presence of residual water in the initial phthalocyanine, the exact composition of the product of the oxidation of Al(Pc)OH by $NO[PF_6]$ is not known.[51] The reaction of Al(Pc)F and Ga(Pc)F with $NO(BF_4)$ and $NO(PF_6)$ proceeds rapidly in dry CH_3NO_2 or CH_2Cl_2 with formation of complexes having the composition $[M(Pc)F]Y_x$, where M = Al, Y = $[PF_6]$, and x_{max} = 0.9 or M = Ga, Y = $[PF_6]$, and x_{max} = 0.9. These compounds are thermally stable up to 110 °C; in a stream of dry nitrogen the decomposition begins at 125 °C.

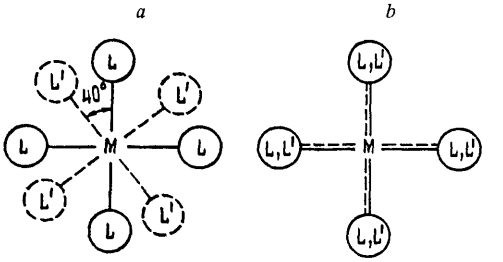


Figure 10. The arrangement of the ligands in the stack: *a*) 40° displacement; *b*) 0° displacement.

A characteristic feature of these compounds is their stability on prolonged exposure to atmospheric oxygen. Thus the conductivity of the complex $\{[Al(Pc)F][PF_6]_{0.59}\}_n$ diminished by 0.1 Ω^{-1} cm^{-1} after it had been kept in air for a month, while that of the complex $\{[Al(Pc)F][BF_4]_{0.44}\}_n$ remained unchanged at 3×10^{-2} Ω^{-1} cm^{-1} after it had been kept for a year in the air. This feature is the opposite of the behaviour of the complexes $[M(Pc)F]_n$ oxidised by iodine,[88] which lose iodine with time. Thus, although the conductivity

of polyfluorometallophthalocyanines oxidised with $NO[BF_4]$ or $NO[PF_6]$ is ten times lower than that of $\{[M(Pc)F]I_x\}_n$, they are of considerable interest in view of their high stability.[89]

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The partial oxidation of metallophthalocyanines and porphyrins is an important chemical method for the preparation of new synthetic metals. Elemental iodine, which has a large number of reduced forms, is used as a convenient reductant more frequently than others.

The ligands play the main role in the electrical conduction in iodinated metallophthalocyanines and metalloporphyrins. The metal ion in such a complex influences the properties of the ligands but is not involved directly in charge transfer. An exception is $Ni(TBP)I_{1.0}$, in which charge transfer takes place via both the ligands and the metal [in contrast to $Ni(OMTBP)I_x$, $M(TMP)I_{1.0}$, and $NiPcI_{1.0}$, where the charge is transferred only via the organic ligand]. Thus slight changes in the structure of the ligands exert a significant influence on the electrical properties of the system. It is of interest to note that in certain cases homogeneous complex catalysts incorporating a transition metal ion and a ligand with an extensive system of conjugated bonds also transfer an electron to the substrate via the ligand (the so-called peripheral mechanism).[90-92]

It has been shown in relation to the complexes $Ni(OMTBP)I_x$ that a change in the oxidation state does not affect the qualitative character of the dependence of σ on T and influences only the absolute magnitude of the conductivity. One may claim that the interplanar distances in the stacks and the steric disposition of the molecules in the latter play an important role in the conduction process. In other words, by changing these parameters, it is possible to regulate the conductivities of phthalocyanine and porphyrin systems.

In the mid 1970's it was suggested that in the future the importance of phthalocyanines may be extremely significant in fields such as those of one-dimensional conductors and superconductors.[93] There is no doubt that this prediction has come true as regards metallic conductivity. Whether or not superconductors will be obtained on the basis of phthalocyanines remains a problem for further research.

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The Application of Cyclopalladated Compounds in Synthesis

A.D.Ryabov

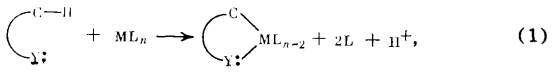
The review is devoted to the application in organic synthesis of organopalladium compounds with an intramolecular coordinate bond. Reactions with alkenes, alkynes, carbon monoxide, isocyanides, organolithium and organomagnesium compounds, and other reagents are examined. The mechanisms of these processes are discussed.
The bibliography includes 129 references.

CONTENTS

I. Introduction 153
II. The synthesis and dissociation of palladocycles 153
III. Reactions with alkenes 155
IV. Reactions with alkynes 160
V. Reactions with carbon monoxide 161
VI. Reactions with isocyanides and carbon dioxide 164
VII. Halogenation 165
VIII. Alkylation, acylation, and phosphination 166
IX. Other reactions 168

I. INTRODUCTION

The discovery of the reactions involving the cyclometallation of organic compounds by transition metal complexes,[1] leading to the formation of transition metal–carbon and metal–donor atom bonds, i.e.



(1)

initiated the wide-scale and comprehensive investigation of cyclometallated molecules. One of the causes of the continuous interest in these substances is the possibility of modelling many catalytic reactions involving transition metal complexes in which the formation of labile metal–carbon bonds has been postulated as the key stages.[2] A large number of cyclometallated complexes have been synthesised in recent years, which has been reflected in review articles.[3-7] The chemistry of cyclometallated compounds† soon outgrew the limits of purely model problems and these complexes have come to be used independently in organic synthesis. Their employment makes it possible to achieve absolute regioselectivity and, in the case of σ-aryl complexes and related compounds, *ortho*-substituted products, which are otherwise difficult to synthesise, can be obtained.

This review summarises the literature data concerning the application of cyclometallated complexes in organic synthesis. Since palladium(II) complexes are most widely used, attention has been naturally concentrated on the reactions of these compounds. The review also includes certain processes which are potentially important for organic synthesis. The methods of synthesis of cyclopalladated complexes as well as procedures for the cleavage of palladium–carbon bonds, leading to the liberation of the organic fragments of the complexes, are briefly described.

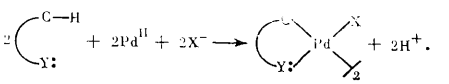
†Cyclopalladated compounds or cyclopalladated complexes have been recently referred to also as palladocycles. All these equivalent terms are used in this review.

II. THE SYNTHESIS AND DISSOCIATION OF PALLADOCYCLES

These problems have been examined in detail in a number of reviews.[3-7] Only general approaches to the synthesis of the cyclopalladated complexes used in organic synthesis are briefly described below. This is done, in particular, also in order to emphasise the availability of the initial compounds of the type of di-μ-chlorobis(cyclometallated ligand)dipalladium(II).

Direct Palladisation

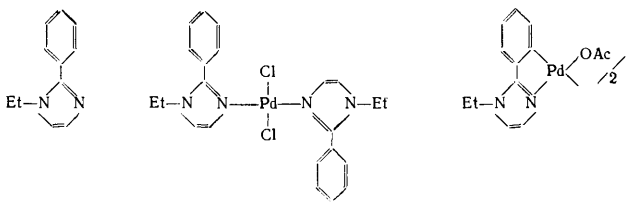
The reaction involves the direct interaction of the organic ligand with palladium(II) salts:



(2)

M_2PdCl_4, M_2PdCl_4–MOAc, and $Pd(OAc)_2$, where M = Li or Na, are used. The palladation is carried out in methanol, ethanol, acetone, dioxan, chloroform, acetic acid, and binary aqueous organic mixtures. As a rule, the palladation reaction takes place smoothly at room temperature, but in a number of instances heating is necessary. The "mildest" metallating agent is lithium or sodium tetrachloropalladate(II); the M_2PdCl_4–alkali metal acetate or amine system is frequently more effective. The acetate anion functions as a general base, which facilitates the dissociation of the C–H bond.[8]

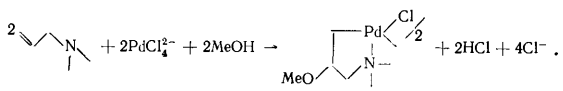
In those cases where the treatment of the ligand with M_2PdCl_4 does not lead to cyclopalladated products (the so-called bisadducts $PdCl_2L_2$ are then usually formed), palladium(II) acetate may prove to be effective. For example, Li_2PdCl_4 reacts with 1-ethyl-2-phenylimidazole(I), giving rise to the bisadduct (II), while the required cyclometallated complex (III) is obtained via the reaction of compound (I) with palladium(II) acetate in boiling acetic acid.[9]



(I) (II) (III)

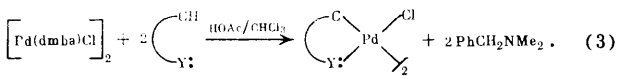
In a number of instances complexes of the type $PdCl_2L_2$ can be converted into cyclopalladated products of the type $[Pd(L-H)Cl]_2$ by heating or treatment with bases (see, for example, Shaw and co-workers[10,11]).

Direct palladation makes it possible to obtain complexes with aromatic, pseudoaromatic, and aliphatic ligands. The last can also be synthesised from allylamines[12] and allyl sulphides[13] by treating them with $PdCl_4^{2-}$ in the presence of nucleophiles:



Ligand Exchange

The essential feature of a recently proposed method[14] consists in the interaction of any *ortho*-palladated complex with the free ligand, which leads to a new palladocycle:



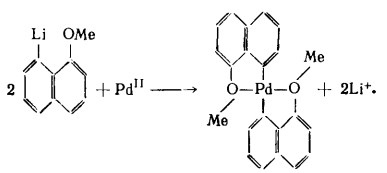
(3)

Here and henceforth $[Pd(dmba)Cl]_2$ represents di-μ-chlorobis(*NN*-dimethylbenzylamine-C^2,*N*)dipalladium(II) $[Pd(C_6H_4CH_2NMe_2)Cl]_2$. Acetic acid is an essential component of the reaction mixture; in its absence there is no exchange. The method makes it possible to obtain complexes with donor N and P atoms; ligands with oxygen-containing donor groups do not react.

This method is particularly convenient for the synthesis of compounds which can be obtained by the direct palladation of the corresponding ligands, in particular for the synthesis of di-μ-chlorobis(*N*,*N*-diethyl-4-nitrobenzylamine-C^2,*N*)-dipalladium(II).[14]

Transmetallation

The method consists in the treatment of the ligand with a suitable organolithium compound, which gives rise to the lithio-derivative of the latter, to which the metal salt is then added. Complexes of 1-methoxynaphthalene are synthesised in this way, for example:[15]



The use of organolithium compounds for such purposes has been considered in detail in a review.[5]

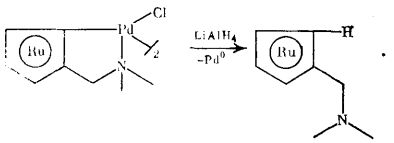
Another promising method involves the interaction of organomercury compounds with zerovalent palladium complexes of the type $Pd(PPh_3)_4$ or Pd_2(dibenzylideneacetone)$_3$.[16,17] These reactions proceed via the oxidative addition mechanism; two reviews are devoted to their characteristics.[18,19]

Thus it follows from the above discussion that cyclopalladated compounds are fairly readily available; they are stable in air and can be stored indefinitely. All these factors create conditions for the application of these complexes in organic synthesis.

Processes accompanied by the dissociation of the metal–carbon σ-bond in the metallocycle are no less important because in many instances the interaction of the initial complex with any substrate leads to the formation of a new complex with a modified cyclometallated organic ligand. In order to use such processes in synthesis, it is necessary to have at ones disposal selective methods which make it possible to decompose the metallocycles in such a way that the modified organic ligand can be readily isolated. Some of these methods are described below.

Reduction with Lithium Tetrahydroaluminate

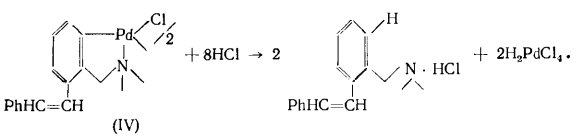
In organic solvents, for example in dry diethyl ether, the reduction of palladocycles by $LiAlH_4$ leads to the formation of the free ligand and zerovalent palladium, as happens, in particular, in the case of a ruthenocene derivative:[20]



The use of $LiAlD_4$ leads to selective deuteriation. $NaBH_4$ and H_2 are used as other reductants.

Acidolysis

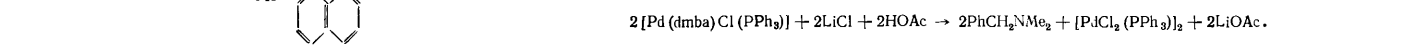
The palladium–carbon bond in the compounds considered dissociates in the presence of strong protic acids of the type of HCl, $HClO_4$, HNO_3, etc. For example, treatment of compound (IV) with hydrochloric acid in aqueous dioxan solution leads to the formation of the free ligand and the $PdCl_4^{2-}$ anion:[21]



(IV)

Acidolysis in Acetic Acid Induced by the Chloride Ion

As a rule, dimeric cyclopalladated compounds do not decompose in acetic acid. However, the monomeric complexes, i.e. the products of the cleavage of the chloride bridges by triphenylphosphine, undergo acidolysis in acetic acid in the presence of LiCl:[22,23]



This results in the formation of an insoluble palladium(II) complex and the free ligand. The *ortho*-deuteriated products are obtained in DOAc.[23]

III. REACTIONS WITH ALKENES

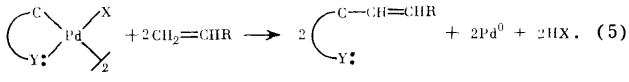
The possibility of the interaction of the cyclopalladated complexes with alkenes, involving the formation of the products of the formal substitution of palladium(II) by the vinyl group, was indicated for the first time in a review,[24] whose author concluded that styrene reacts readily with $[Pd(dmba)Cl]_2$ in acetic acid at room temperature with formation of 2-dimethylaminomethylstilbene:

$$[Pd(dmba)Cl]_2 + 2PhCH{=}CH_2 \rightarrow 2o\text{-}Me_2NCH_2C_6H_4CH{=}CHPh + 2Pd^0 + 2HCl. \quad (4)$$

This communication was followed by a large number of reports devoted to the reactions of palladocycles with alkenes; the results of these studies are summarised in Table 1.

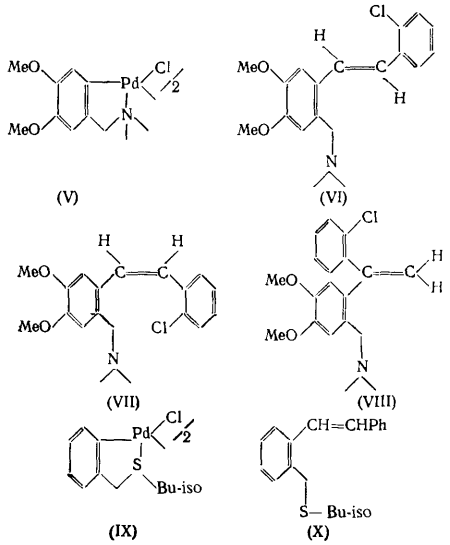
The Stoichiometry and Products of the Reaction

The reactants interact in molar proportions of 1:1, i.e. one palladocycle reacts with one alkene molecule:



(5)

Reactions of type (5) are oxidation-reduction processes and are accompanied by the reduction of palladium(II) to zerovalent palladium. Only α-olefins react. The process proceeds stereospecifically: palladium is substituted by the α-carbon atom of the alkene and the product has the *E*-configuration. This is indicated by the spin–spin coupling constants of the olefin protons $^3J(HH)$, which amount to 15–17 Hz.[25] The infrared spectra of the products contain the band due to the deformation vibrations of the *trans*-HC=CH bonds at 950–990 cm^{-1}.[21] The only exception known hitherto is that of the reaction of compound (V) with *o*-chlorostyrene.[25] In this case the *Z*-stilbene (VII) and 1,1-diarylethylene (VIII) are obtained together with the main product (VI). However, the amount of the last two impurities does not exceed 5% of the content of the main product (VI). The impurities can be readily removed by recrystallising the corresponding hydrochlorides from ethanol:



(V) (VI) (VII) (VIII) (IX) (X)

Table 1. Vinylation of cyclopalladated complexes.

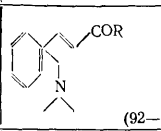
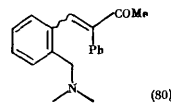
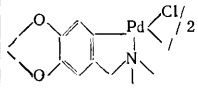
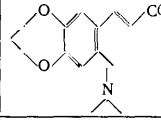
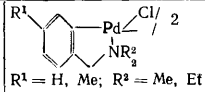
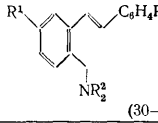
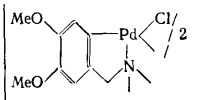
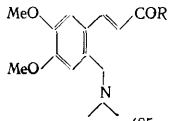
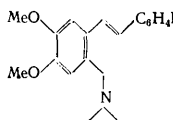
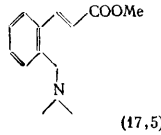
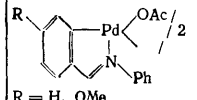
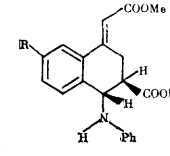
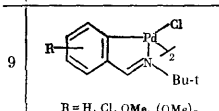
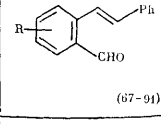
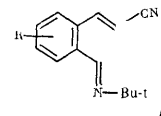
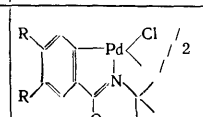
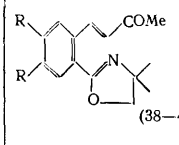
No.	Complex	Alkene	Product (yield, %)	Refs.
1	$[Pd(dmba)Cl]_2$	$H_2C{=}CHCOR$ R = Me, Et, C_6H_{11}	 (92–96)	[28]
2	ditto	$H_2C{=}C(Ph)COMe$	 (80)	[28]
3		$H_2C{=}CHCOMe$		[28]
4	 R^1 = H, Me; R^2 = Me, Et	$H_2C{=}CHC_6H_4R^3\text{-}n$ R^3 = H, Me, OMe, Cl, Br	 (30–60)	[21]
5		$H_2C{=}CHCOR$ R = Me, OEt	 (85–98)	[25]
6	ditto	$H_2C{=}CHC_6H_4R$ R = H, *p*-OMe, *o*-, *m*-, or *p*-Cl, *o*-, *m*-, or *p*-NO_2	 (32–94)	[25]
7	$[Pd(dmba)OAc]_2$	$H_2C{=}CHCOOMe$	 (17,5)	[37]
8	 R = H, OMe	ditto	 (10–11)	[37]
9	 R = H, Cl, OMe, $(OMe)_2$	$H_2C{=}CHPh$	 (67–91)	[43]
10	ditto	$H_2C{=}CHCN$	 (78)	[42]
11	 R = H, OMe	$H_2C{=}CHCOMe$	 (38–45)	[115]

Table 1 (cont'd).

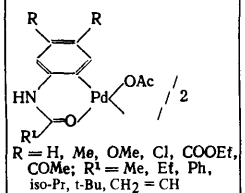
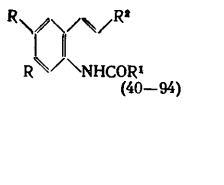
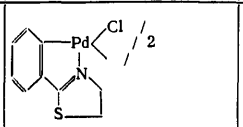
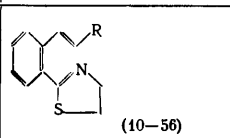
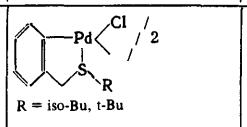
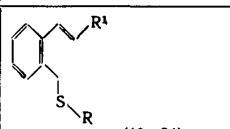
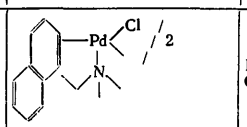
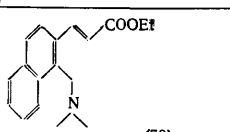
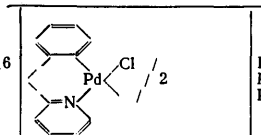
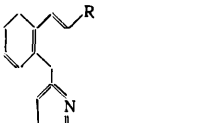
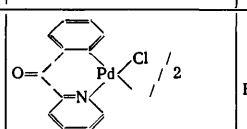
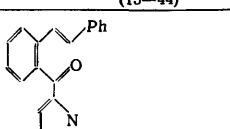
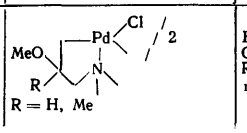
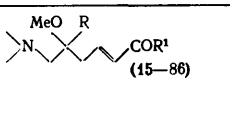
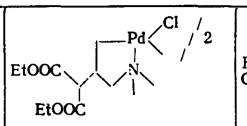
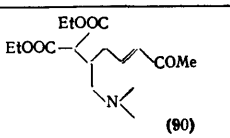
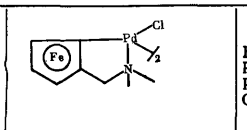
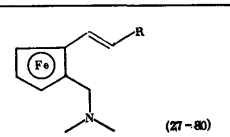
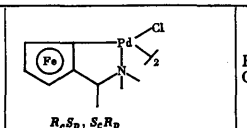
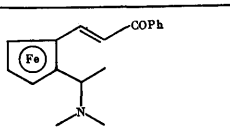
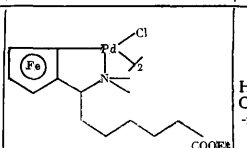
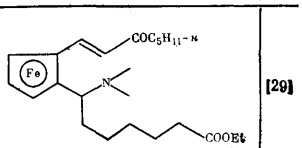
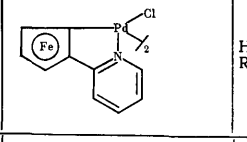
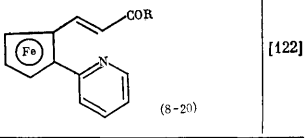
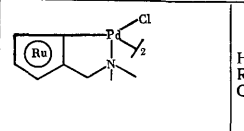
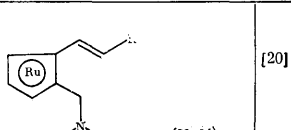
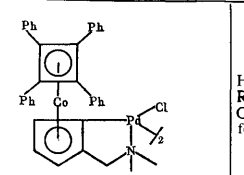
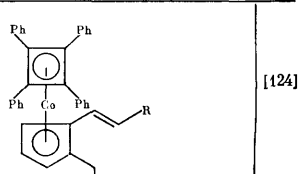
No.	Complex	Alkene	Product (yield, %)	Refs.
12	 R = H, Me, OMe, Cl, COOEt, COMe; R^1 = Me, Et, Ph, iso-Pr, t-Bu, CH_2 = CH	H_2C=CHR^2 R^2 = H, Ph, CN, COOMe, OAc, $CH(OEt)_2$, 3,4-$OCH_2OC_6H_3$, 3-AcO-4-MeO-C_6H_3	 (40—94)	[36, 116]
13		H_2C=CHR R = COMe, Ph	 (10—56)	[117]
14	 R = iso-Bu, t-Bu	H_2C=CHR^1 R^1 = COMe, Ph	 (10—21)	[26]
15		H_2C=CHCOOEt	 (70)	[118]
16		H_2C=CHR R = COMe, Ph	 (13—44)	[119]
17		H_2C=CHPh		[120]
18	 R = H, Me	H_2C=$CHCOR^1$ R^1 = Me, Et, n-C_6H_{13}, OEt	 (15—86)	[34]
19		H_2C=CHCOMe	 (90)	[121]
20		H_2C=CHR R = COMe, Ph, CN, CO_2Et, COPh	 (27—80)	[122, 123]
21	 R_cS_p, S_cR_p	H_2C=CHCOPh		[65]

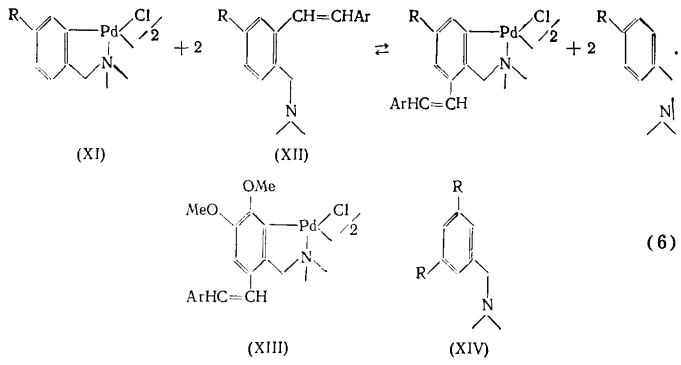
Table 1 (cont'd).

No.	Complex	Alkene	Product (yield, %)	Refs.
22		H_2C=$CHCOC_6H_{11}$-n	 (61)	[29]
23		H_2C=CHCOR R = Me, Ph	 (8-20)	[122]
24		H_2C=CHR R = COMe, COPh, Ph	 (89-94)	[20]
25		H_2C=CHR R = H, Ph, COMe, COPh, ferrocenyl	 (30-57)	[124]

The reaction of [Pd(ba)OAc]$_2$(di-μ-acetatobis(benzylidene-aniline-C^2,N)-dipalladium(II) [Pd(C_6H_4CH=NPh)OAc]$_2$ with methyl acrylate (Table 1, No. 8) exhibits a different stoichiometry, namely one palladocycle reacts with two molecules of the alkene. The structure of the reaction product was established in this case by X-ray diffraction.[37]

The side products in this reaction are most frequently the free ligands formed as a result of the dissociation of the initial complexes. For example, in the interaction of the complex (IX) with styrene in boiling *o*-xylene in the presence of NEt_3 the yields of *trans*-2-(isobutylthiomethyl)-stilbene (X) and $PhCH_2SBu$-iso are 21 and 76% respectively.[26] In acetic acid there is also a possibility of the secondary palladation of the arylolefins formed. Thus the reaction of compound (XI) with *para*-substituted styrenes in an acetic acid–benzene mixture involves the formation, together with the free stilbenes (Table 1, No. 4), of the palladation products of the latter (XII).[21] The complexes (XII) are obtained either as a result of the direct palladation of stilbenes by palladium(II) or as a result of the ligand exchange [reaction (6)]. The exchange reaction, whose nature is analogous to that of reaction (3), explains the

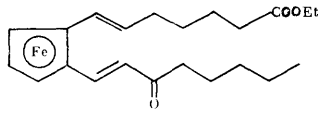
appearance of free ligands in acetic acid media:[21]



(6)

Reaction (6) leads to the non-productive consumption of the initial complex and to a decrease of the yield of the final product. Its suppression increases the yields of stilbenes.[25] In the reactions of compounds (V) with styrenes the hypothetical complex (XIII) can hardly exist for purely steric reasons, since the products of the palladisation of 3,5-dialkylbenzyl-*NN*-dimethylamines (XIV), containing Pd–C bonds in the *ortho*-position relative to the alkyl substituent, do not exist.[27]

The causes of the formation of the free ligands in the absence of acetic acid are less understandable. It has been assumed that[28] they are obtained as a result of the cleavage of the Pd–C bonds in the initial complexes under the influence of the hydrochloric acid liberated in the course of reaction (5), since in the presence of tertiary amines, which are potential HCl acceptors, the free ligands are not formed. However, subsequently, for example, in the study of Fuchita et al.[26], it was shown that the dissociation takes place also in the presence of amines. The role of the latter in reaction (5) remains altogether obscure. This is further confirmed by the formation of the product (XV) in 10% yield on ketovinylation of the ferrocene derivative (Table 1, No. 22) in the absence of NEt_3.[29]



(XV)

Overall, reaction (5) is a variant of the familiar reactions involving the arylation of olefins by hydrocarbons (the Fujiwara–Moritani reaction)[30,31] or organometallic compounds (the Heck reaction)[32,33] in the presence of palladium(II) salts:

$$ArM + H_2C{=}CHR + Pd^{II} \rightarrow ArHC{=}CHR + M^+ + H^+ + Pd^0, \qquad (7)$$

where M = H or HgX. As in reaction (5), the aryl group adds to the least branched carbon atom involved in the double bond and the product has the *E*-geometry. Thus reaction (5) can serve as a convenient model of the Fujiwara–Moritani or Heck processes, in which the initial complex contains a stable palladium–carbon bond.

The Nature of the Cyclopalladised Complex and the Olefin

Table 1 shows that a whole series of palladocycles with chelating donor atoms of different types (Table 1, Nos. 1–17) react with olefins. Derivatives of *NN*-dialkylbenzylamines (Table 1, Nos. 1–7), benzylideneamines, and anilines (Nos. 8–10) have been studied in greatest detail. The donor atoms in the reacting complexes are those of nitrogen, oxygen, and sulphur. Five- and six-membered palladocycles react. The aliphatic complexes with a nitrogen donor atom also enter into the reaction (Table 1, Nos. 18 and 19), while the analogous complexes with an S donor atom in the ring are unreactive.[34] Palladocycles such as ferrocene, ruthenocene, and cyclopentadienyltetraphenylcyclobutadienecobalt derivatives (Table 1, Nos. 20–25) also react readily with olefins. The possibility of the asymmetric palladation of these compounds[35] creates conditions for the synthesis of enantiomeric and diastereoisomeric vinyl compounds (Table 1, Nos. 21 and 22).

As mentioned above, only α-olefins undergo reaction (5). Branched alkenes, for example pent-3-en-2-one, do not interact with $[Pd(dmba)Cl]_2$. On the other hand, the terminal alkene 3-phenylbut-3-en-2-one reacts and the yield is 80%.[28] Substituents at the double bond exert a weak influence on the yields of the vinylation products (see, for example, Horino and Inoue[36]). On the whole, the yields are determined more by the nature of the initial complex than by that of the alkene. As a rule, if reaction (5) involving any alkene proceeds with a satisfactory yield then it also proceeds fairly smoothly with other alkenes of different types. The exceptions are the $[Pd(dmba)Cl]_2$ analogues already mentioned. These complexes react readily with vinyl ketones (Table 1, Nos. 1–3 and 5) in boiling benzene or toluene in the presence of tertiary amines but under these conditions they are inert with respect to olefins without keto-groups.[21,25,37]

The vinylation of *NN*-dialkylbenzylamine complexes by these alkenes can be carried out only in the presence of carboxylic acids; it has been noted that the reaction is significantly accelerated in the presence of sodium or lithium perchlorate.[21]

Reaction Conditions

Reaction (5) is usually carried out with an aromatic hydrocarbon as the solvent (benzene, toluene, and xylenes) in the presence of a tertiary amine, usually NEt_3 (method A), or in acetic acid to which benzene or methylene chloride are added to increase the solubility of the initial complexes (method B). The reaction is performed at 75 °C and above by method A and at lower temperatures by method B. The reaction time is determined by the nature of the initial palladocycle and can vary within wide limits. As a rule,[21,25,28] the vinylation of benzylamine derivatives is accelerated in the presence of acetic acid but sometimes the reaction does not proceed in this solvent.[34]

The rates of reactions catalysed by acetic acid increase markedly when lithium, sodium, or magnesium perchlorate is added to the acetic acid solutions.[21,38] Their catalytic effect consists in the fact that they react with acetic acid via reaction (8) and the real catalyst of reaction (5) is

perchloric acid:

$$MClO_4 + HOAc \overset{K_s}{\rightleftharpoons} MOAc + HClO_4. \quad (8)$$

The equilibrium in Eqn. (8) is strongly displaced to the left: for $[NaClO_4] = 0.1$ M, the $HClO_4$ concentration is only $\sim 2 \times 10^{-5}$ M ($K_s = 4.3 \times 10^{-9}$ M). The cyclopalladised complexes are stable at such low $HClO_4$ concentrations and do not decompose under these conditions. The addition of small amounts of $HClO_4$ to the reaction mixture also increases the rate of reaction.[38]

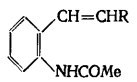
The Synthesis of Analogues of Prostaglandins

Table 1 presents examples of the reactions of alkenes with cyclopalladated complexes isolated beforehand in a pure state. At the same time, it is possible to carry out the vinylation of the palladocycles formed *in situ*. Holton[39] used this approach to synthesise prostaglandins. The palladisation of the enamine (XVI) in a mixture of ethylene-chlorohydrin and dimethyl sulphoxide (DMSO) leads to the bicyclic cyclometallated complex (XVII) with a five-membered palladocycle; without being isolated in a pure state, the latter is treated with n-pentyl vinyl ketone. The vinyl ketone (XVIII) was obtained as a result. It can then be converted by traditional chemical methods[39] into Corey's lactone-diol (XIX), which is a precursor of prostaglandin $PGF_{2\alpha}$.[40]

The ketovinylation of the products of the asymmetric palladation of ferrocene derivatives is also a key stage in the synthesis of models of natural prostaglandins.[29] The metallation of 2-(6-ethoxycarbonyl-1-dimethylaminohex-1-yl)-1-(3-oxo-oct-1-en-1-yl)ferrocene (Table 1, No. 22) with subsequent mild reduction to the methiodide (XX) with $NaBH_4$ leads to compound (XXI).

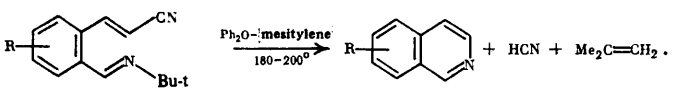
The Synthesis of Heterocycles

The vinylation of *ortho*-palladised compounds, which leads, in particular, to *ortho*-substituted stilbenes, is a convenient method of synthesis of compounds of this class (see, for example, Becker[41]). However, there is an additional interest in analogous products owing to the possibility of their employment to synthesise heterocyclic compounds. Several examples are presented below. Treatment of compound (XXIIa) with concentrated HCl for several minutes results in the formation of quinoline in high yields.[36] Quinaldine and carbostyril respectively have been obtained analogously from compounds (XII, b and c):[36]

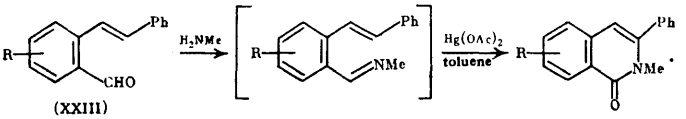


(XXII): a) R=CH(COEt)$_2$; b) R=COMe; c) R=COOMe.

A synthetic approach to substituted isoquinolines, starting with the products of the reactions of *ortho*-palladised Schiff bases with acrylonitrile (Table 1, No. 10), has been proposed recently:[42]

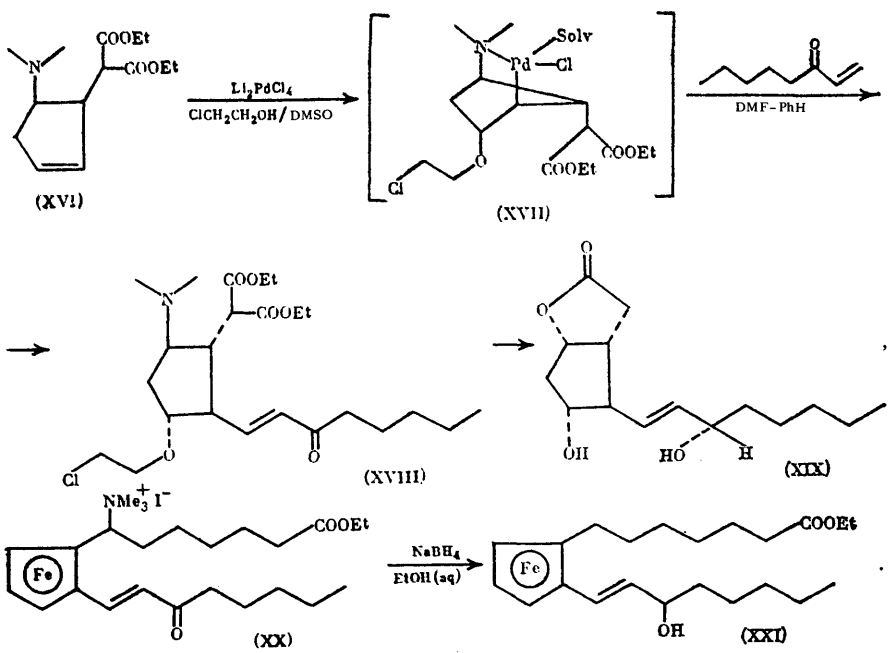


3-Arylisoquinolones can be obtained[43] in accordance with the scheme



(XXIII)

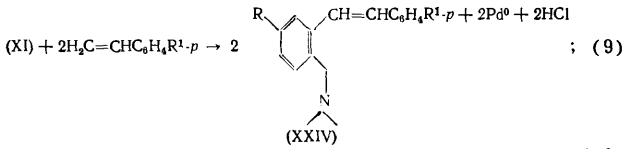
The starting compounds are synthesised as shown in Table 1 (No. 9). The above methods are attractive,



because of their simplicity and the high yield of the required products.

The Reaction Mechanism

The kinetics of the reactions of cyclopalladated complexes with alkenes have been investigated in relation to the interaction of the complex (XI) with *para*-substituted styrenes in acetic acid:[38,44]



$$(XI) + 2H_2C{=}CHC_6H_4R^1\text{-}p \rightarrow 2\ (XXIV) + 2Pd^0 + 2HCl \quad ; \quad (9)$$

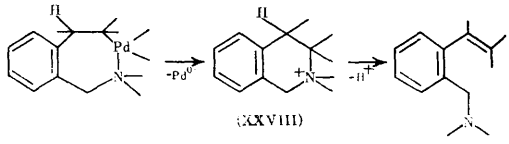
$$d[(XXIV)]/dt = k_2[(XI)][H_2C{=}CHC_6H_4R^1\text{-}p]. \quad (10)$$

The rate of reaction is described by the kinetic equation (10). An interesting feature of reaction (9) is the large positive salt effect. In the presence of tetrabutylammonium, sodium, lithium, and magnesium perchlorates, k_2 increases sharply. The catalytic effect increases in the above series of cations from left to right and the increase reaches almost two orders of magnitude for $[Mg(ClO_4)_2] = 0.1$ M.

It has been shown[38,44] that the effect of the salt is associated with the existence of equilibrium (8) in acetic acid. Perchloric acid catalyses the process in conformity with a kinetic equation of the type $k_2 = k_3 + k_4[HClO_4]$, i.e. the reaction proceeds via two parallel pathways—the "solvolytic" pathway (k_3) and the acid-catalysed pathway (k_4). Since reaction (9) does not occur in the absence of acetic acid, it is assumed that the solvolytic pathway is promoted by acetic acid. The electrophilic catalyst E (acetic and perchloric acids for the k_3 and k_4 pathways respectively) interacts with the bridging chloro-ligands of the initial complex [Eqn. (11)], which facilitates the coordination of palladium(II) to the alkene molecule:

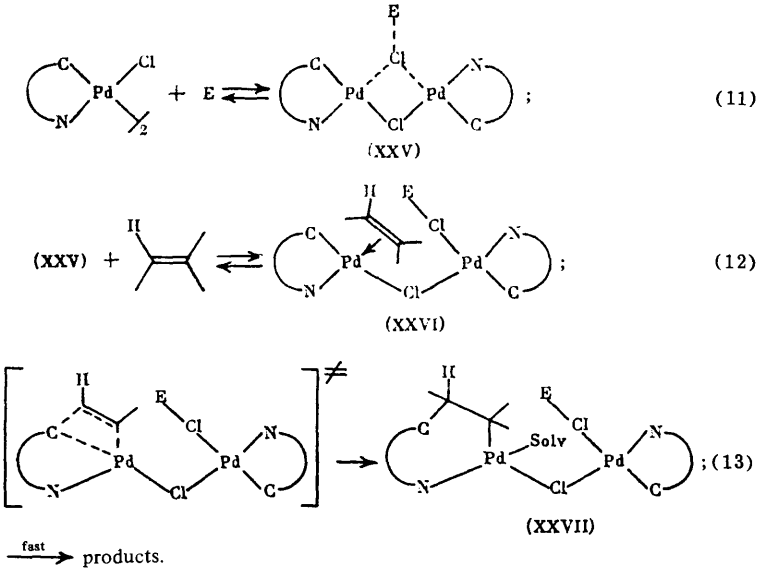
Generally speaking the intermediate complex (XXV) can have only one bridging ligand: similar compounds have been recently characterised by X-ray diffraction methods.[45] Subsequently compound (XXV) reacts reversibly with the alkene to form the π-complex (XXVI). The latter undergoes the rate-limiting π-σ rearrangement via a cyclic four-centre transition state. This is indicated by the low absolute values of the Hammett parameters $\rho(R^1)$ and $\rho(R)$ obtained, which do not exceed unity, and also by the low enthalpies of activation $\Delta H^{\neq}$.[38]

The elimination of hydrogen from the intermediate complex (XXVII), which leads to the final products, is a rapid stage. This is indicated by the kinetic isotope effect $k_2(PdCHCH_2)/.k_2(PhCHCD_2) = 1$. It has been suggested[25,38] that hydrogen is removed in the form of palladium hydride HPd^+ as a result of 1,3-elimination. The same mechanism operates in the Fujiwara–Moritani and Heck reactions [see Eqn. (7)].[46–48] Another possibility for the conversion of the complex (XXVII) into the reaction product involves the reductive elimination of zerovalent palladium, which leads to tetrahydroisoquinoline derivatives of type (XXVIII). The latter are fairly labile and readily undergo the Hofmann rearrangement to arylolefins in the presence of bases:[49]



(XXVIII) (14)

The mechanism (11)–(13) is probably valid in broad outline also for other palladocycles. There may be differences in the method of incorporation of the alkene in the coordination sphere of palladium(II). The olefin can in principle substitute the donor atom in cyclopalladated complexes, which results in their dechelation. Unfortunately, it is difficult to distinguish this possibility by direct kinetic methods from the reaction pathway examined above.



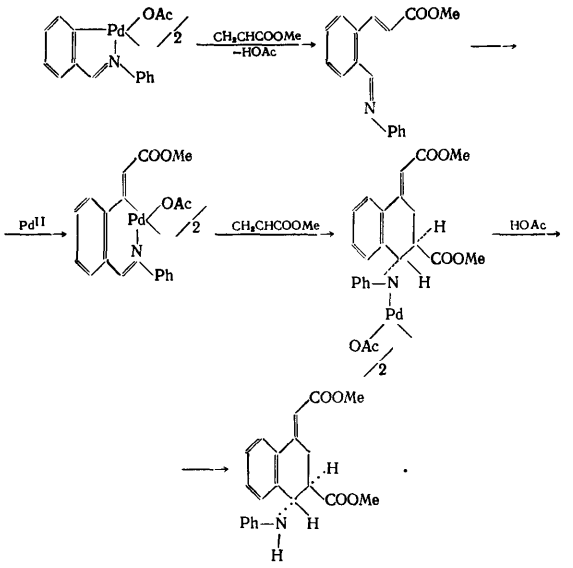
(XXV) (11)

(XXVI) (12)

(XXVII) (13)

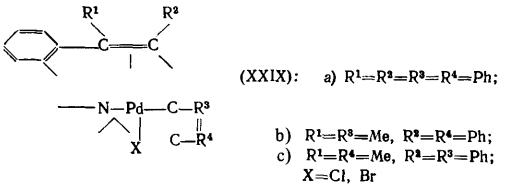
(XXVII) $\xrightarrow{fast}$ products.

In conclusion we shall consider the "double" insertion mechanism[37] (Table 1, No. 8). The usual formation of the arylolefin is followed by its secondary vinyl palladation. Next comes the insertion of a second methyl acrylate molecule and intramolecular addition of the palladium–carbon bond to the C=N double bond. Finally the Pd–N covalent bond formed undergoes homolysis or acidolysis by the acetic acid, which appears in the course of the first vinylation stage:[37]

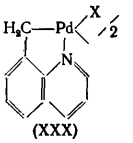


IV. REACTIONS WITH ALKYNES

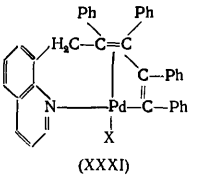
Cyclopalladised compounds readily react with disubstituted alkynes of the type $RC{\equiv}CR'$ ($R = R' = Ph$; $R = Ph$, $R' = Me$), forming double insertion products.[50] For example, $[Pd(dmba)Cl]_2$ is then converted into the complex (XXIXa) with a rarely encountered nine-membered palladocycle. The asymmetric alkyne PhC_2Me gives rise to a mixture of the isomeric complexes (XXIXb) and (XXIXc), each of which has been isolated in a pure state:



(XXIX): a) $R^1=R^2=R^3=R^4=Ph$;
b) $R^1=R^3=Me$, $R^2=R^4=Ph$;
c) $R^1=R^4=Me$, $R^2=R^3=Ph$;
X=Cl, Br

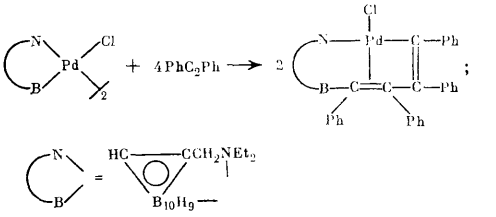


(XXX)

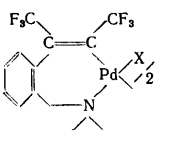


(XXXI)

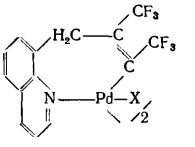
The structure of compounds (XXIXb, X = Br) and (XXIXc, X = Cl) has been established by X-ray diffraction. Tolane reacts with compound (XXX), also giving rise to the double insertion product (XXXI); hexaphenylbenzene is formed as a side product. The yield of compound (XXXI) depends on the reaction time and it has been assumed on this basis[50] that the complex (XXXI) can be an intermediate in the trimerisation of tolane. The reaction of compound (XXX) with PhC_2Me leads to a mixture of 1,2,4-trimethyl-3,5,6-triphenylbenzene and 1,3,5-trimethyl-2,4,6-triphenylbenzene in proportions of 7:3; the yield of the analogue (XXXI) does not exceed 1% in this case.[50] Double insertion products are also formed in the interaction of tolane with the *B*-palladated *o*-carbaborane:[51]



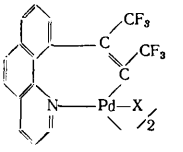
Cyclopalladised derivatives of benzo[*h*]quinoline, azobenzene, and *NN*-dimethyl-1-naphthylamine do not react with PhC_2Ph.[50] Nor has it been possible to obtain the products of the insertion in the Pd–C bond of one PhC_2Ph molecule. On the other hand, in the case of hexafluorobut-2-yne the monoinsertion products (XXXII)–(XXXV) are formed exclusively.[50,52,53]



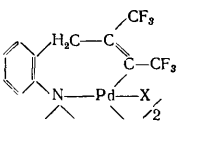
(XXXII)



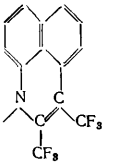
(XXXIII)



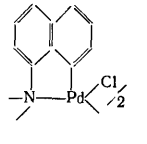
(XXXIV)



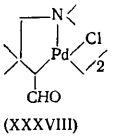
(XXXV)



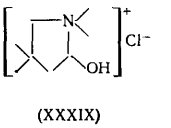
(XXXVI)



(XXXVII)



(XXXVIII)



(XXXIX)

The unusual compound (XXXVI), obtained as a result of the dissociation of the N–Me bond, has been isolated in the reaction of compound (XXXVII) with $CF_3C_2CF_3$.[50] Tolane does not react with the aliphatic cyclopalladated complex (XXXVIII), but treatment of the latter with phenylacetylene leads to 3,3-dimethyl-4-dimethylaminobutanal, whose hydrochloride has the cyclic structure (XXXIX).[54]

The reactions examined in this Section lead in most cases to new palladocycles and only sometimes to new free organic compounds. However, all these processes are extremely promising, since their products are difficult to obtain by other methods. We may note that, whereas the vinylation of palladated ligands (Section III) is characteristic of palladium(II) compounds only, the insertion of alkynes is also observed for other cyclometallated complexes of platinum group metals. In particular PhC_2Ph gives rise to the complex $\{\overline{Rh[(PhC=CPh)_2C_6H_4PPh_2]}PPh_3\}$,[55,56] while $CF_3C_2CF_3$ produces $\{\overline{Ru[(CF_3C=CCF_3)_2C_6H_4PPh_2]}(\eta\text{-}C_5H_5)\}$,[57] i.e. complexes with eight-membered metallocycles are formed.

There are no data concerning the mechanisms of the interaction of alkynes with palladocycles. However, the mechanism of the double insertion of PhC_2Ph, leading to compounds of type (XXIX), is probably of special interest. The fact that it has not been possible[50] to detect the mono-insertion products suggests the possibility of the synchronous addition of two alkyne molecules to the palladium–carbon bond.

V. REACTIONS WITH CARBON MONOXIDE

The ability of carbon monoxide to react with compounds containing metal–carbon bonds is well known (see, for example, the relevant reviews[58,59]). Cyclopalladated complexes, to the reactions of which with CO this Section is devoted, are not exceptional.

Table 2. Carbonylation of cyclopalladated complexes.

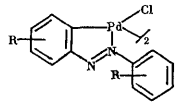
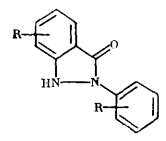
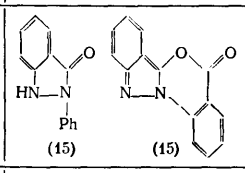
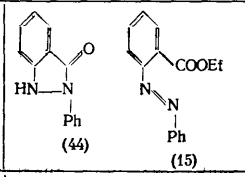
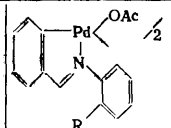
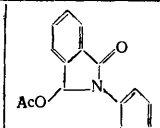
No.	Complex	Product (yield, %)	Solvent (p_{CO}, atm)	Refs.
1	 R = H; 2-, 3-, 4-Me; 3-, 4-Cl; 4-OMe	 (55–97)	EtOH, H_2O (30–150)	[61]
2	$[Pd(azb)Cl]_2$	ditto (17)	MeOH (2.8)	[125]
3	$[Pd(azb)OAc]_2$	 (15) (15)	PhCl (1)	[60]
4	ditto	 (44) (15)	EtOH (1)	[60]
5	 R = H, Me	 (65–66)	xylene (1)	[60]

Table 2 (cont'd).

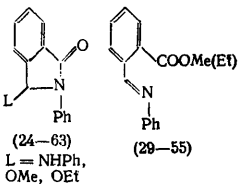
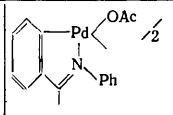
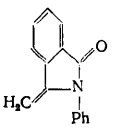
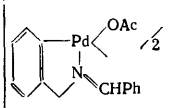
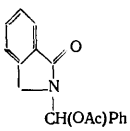
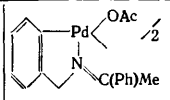
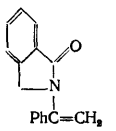
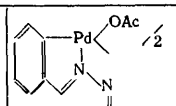
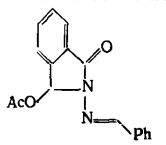
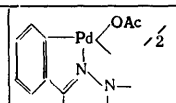
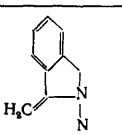
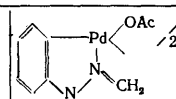
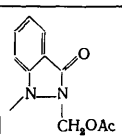
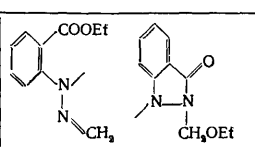
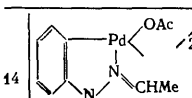
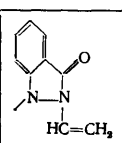
No.	Complex	Product (yield, %)	Solvent (p_{CO}, atm)	Refs.
6	$[Pd(ba)OAc]_2$	 (24–63) L = NHPh, OMe, OEt (29–55)	xylene–aniline, MeOH, EtOH (1)	[60]
7		 (86)	xylene (1)	[60]
8		 (48)	ditto	[60]
9		 (49)	ditto	[60]
10		 (48)	ditto	[60]
11		 (61)	ditto	[60]
12		 (53)	ditto	[60]
13	ditto	 (38) (13)	EtOH	[60]
14		 (68)	PhH	[60]

Table 2 (cont'd).

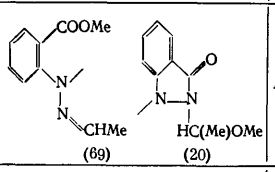
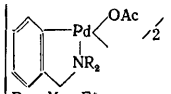
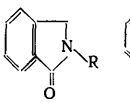
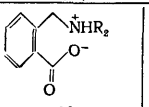
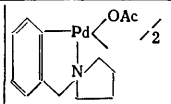
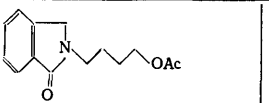
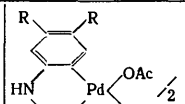
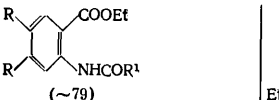
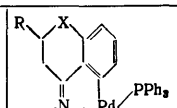
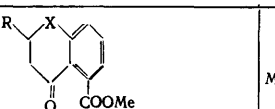
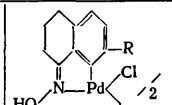
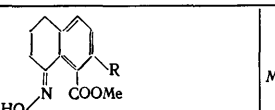
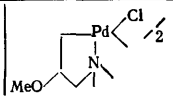
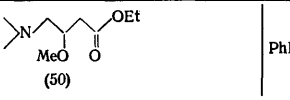
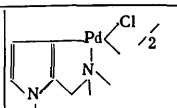
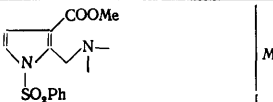
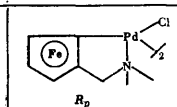
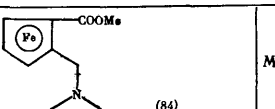
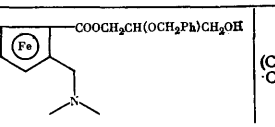
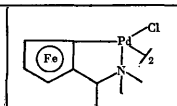
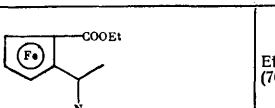
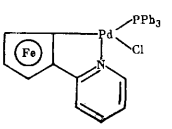
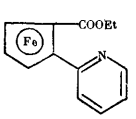
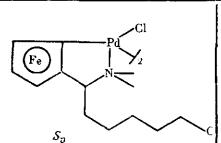
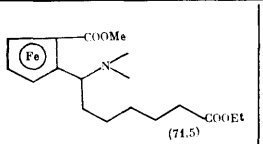
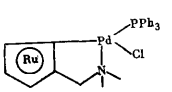
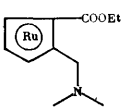
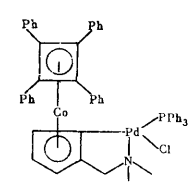
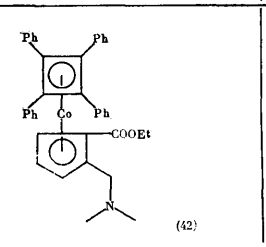
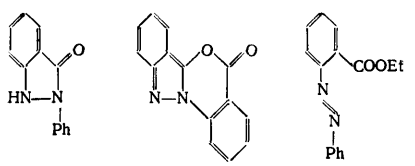
No.	Complex	Product (yield, %)	Solvent (p_{CO}, atm)	Refs.
15	ditto	 (69) (20)	MeOH	[60]
16	 R = Me, Et	 (27—72)  (5—36)	xylene	[60]
17		 (51)	ditto	[60]
18	 R = H, Me, OMe, Cl, COOEt, COMe, COOMe; R^1 = Me, Et, t-Bu	 (~79)	EtOH (1)	[36]
19	 X = O, S; R = H, Me, Ph	 (28—45)	MeOH (60)	[67]
20	 R = H, Et	 (32—73)	MeOH (7)	[63]
21		 (50)	PhH—EtOH	[126]
22		 (69)	MeOH	[128]
23		 (84)	MeOH	[92]
24	ditto		$(CH_2OH)_2$· ·$CH(OCH_2Ph)$	[35]
25		 (20-25)	EtOH, PPh_3 (70)	[65]

Table 2 (cont'd).

No.	Complex	Product (yield, %)	Solvent (p_{CO}, atm)	Refs.
26		 (37)	EtOH (60)	[66]
27		 (71.5)	MeOH	[127]
28		 (40)	EtOH (80)	[20]
29		 (42)	EtOH (50)	[124]

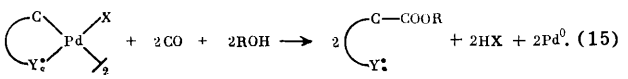
The Stoichiometry and Products of the Reactions

Examples of the reactions of cyclopalladated complexes with carbon monoxide are presented in Table 2. As a rule, one palladocycle absorbs one CO molecule. The carbonylation is accompanied by the reduction of palladium(II) to zerovalent palladium. In contrast to the reactions with alkenes, which yield isotypical compounds, the structure of the products of the carbonylation of palladocycles cannot always be predicted unambiguously. For example, depending on the carbonylation conditions, the products (XL)–(XLII) are formed from the *o*-metallated azobenzene[60,61] (Table 2, Nos. 2–4).



(XL) (XLI) (XLII)

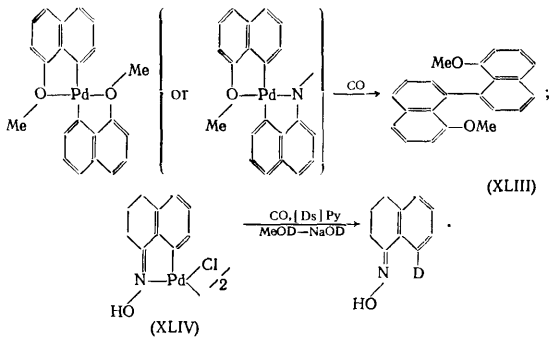
We may note that the formation of the lactone (XLI) is a fairly rare instance of a reaction with the stoichiometry palladocycle : CO = 1 : 2. The same large assortment of products is formed from palladated derivatives of benzilideneaniline (Table 2, Nos. 5–7). Table 2 shows that specific products are formed as a rule from each concrete complex. The most characteristic carbonylation pathway involves the formation of esters in alcohols:



(15)

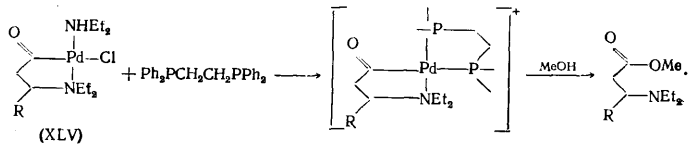
Esters are obtained from cyclopalladated azobenzenes (Table 2, No.4), benzylideneanilines (No.6), the 1-methyl-1-phenylhydrazones of formaldehyde (No.13) and acetaldehyde (No.15), acetanilides (No.18), certain oximes (Nos.19 and 20), aliphatic compounds (No.21), pyrroles (No.22), ferrocene (Nos.23–27), ruthenocene (No.28), and cyclopentadienyltetraphenylcyclobutadienecobalt (No.29).

In a number of instances the "carbonylation products" of palladocycles do not contain carbon monoxide at all. Thus the carbonylation of derivatives of 1-methoxynaphthalene results in the quantitative formation of 8,8′-dimethoxy-1,1′-binaphthyl (XLIII).[15] The study of the interaction of palladated oximes with CO showed[62,63] that the free ligand is formed under certain conditions. This "reductive carbonylation" reaction has served as the basis of a method of synthesis of selectively deuteriated vinyl[62] and aryl[63] oximes. For example, the reaction of the palladocycle (XLIV) with CO in solution in MeOD in the presence of [D_5]pyridine leads to the selective formation of the oxime of 8-deuterio-1-tetralone.[63] This method has advantages over the traditional procedure involving the reduction of $LiAlD_4$ in which the palladised oximes are reduced to amines:[64]



Carbonylation Conditions

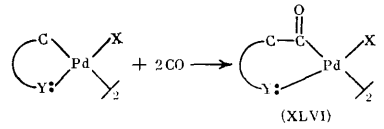
Depending on the nature of the initial palladocycle and the character of the products expected, the following solvents are used: benzene, chlorobenzene, xylenes, methanol, ethanol, water, and a xylene–aniline mixture. A wide range of carbon monoxide pressures are used: from simple bubbling with CO at atmospheric pressure to 150 atm. The reaction time and temperature are also varied within wide limits. The carbonylation is carried out under homogeneous and heterogeneous (when the solubility of the initial complex is low) conditions, sometimes in the presence of triphenylphosphine. It might have been supposed that PPh_3 is necessary to increase the solubility of the initial palladocycles as a result of the formation of soluble monomeric complexes of the type [Pd(L–H)Cl(PPh_3)];[65] however, in a number of instances even homogeneous carbonylation does not take place in the absence of the PPh_3 [66,67] and the conversion of the acyl complex (XLV) into an ester in MeOH takes place only in the presence of $Ph_2PCH_2CH_2PPh_2$.[68] These examples show that phosphines can play an important role in the carbonylation process.



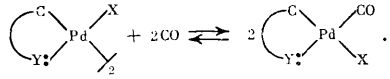
The Reaction Mechanisms

The kinetics of the carbonylation of cyclopalladated compounds have been investigated. The majority of the mechanisms of the interaction with CO postulated are based on the structure of the final products, i.e. the proposed schemes merely clarify the pathways leading to the formation of the final compounds. However, since the majority of similar stages with participation of CO have been thoroughly investigated for other related systems (see, for example, Refs.58, 59, and 69), the reaction mechanisms appear on the whole to be fairly convincing.

Evidently the key stage in all the reactions listed in Table 2 is the insertion of CO in the palladium–carbon σ-bond, which results in the formation of a six-membered cyclic acyl complex (XLVI).



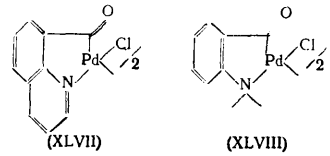
(16)



(17)

The insertion can be preceded by the equilibrium stage involving the rupture of the bridging ligands in accordance with Eqn.(17). Such monomeric cyclopalladated complexes with CO have been described for derivatives of certain oximes and 8-methylquinoline.[70–72] However, in these cases they are not converted further either into compound (XLVI) or into carbonylation products.

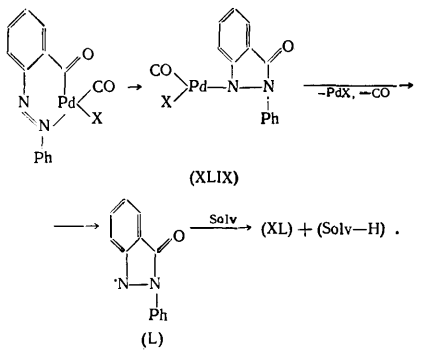
The five-membered acyl complexes (XLVII) and (XLVIII) are known and are obtained by the direct palladisation of the corresponding aldehydes on treatment with Na_2PdCl_4 in ethanol.[73] The reactions of the alkenes RHC $=CH_2$ (R = H, Me, or Et) with $PdCl_2(PhCN)_2$ in the presence of CO and diethylamine lead to the analogous complexes (XLV).[68,74] The increased stability of the complexes (XLV), (XLVII), and (XLVIII) can be accounted for by the presence of the stable five-membered palladocycle:



In particular, compound (XLV) undergoes further reactions only under special conditions[68] (see above). Six- and seven-membered acyl complexes of palladium(II) are significantly less stable and spontaneously enter into further reactions whose sequence is determined by the nature of the initial complex and the medium. Thus stage (16), which is common to all the complexes, is followed by processes typical for the compounds of the given type. We shall consider certain examples.

1. *Palladated azobenzenes.* At high CO pressures (up to 150 atm) in ethanol, 2-aryl-3-indazolinones (XL) are formed preferentially, apparently as a result of the intramolecular addition of the palladium–acyl fragment to the N=N double bond in the intermediate acyl complex, which leads to the amide complex (XLIX).[61] The latter can be converted into the final product (XL) either in the course of the protolysis of the Pd–N bond by ethanol or during

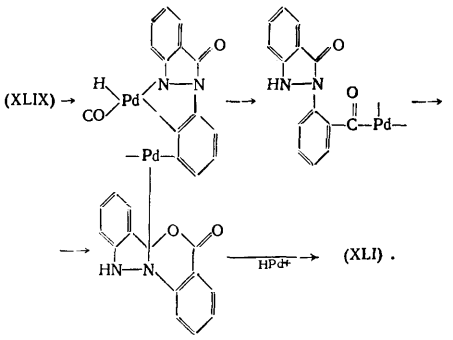
the "oxidative homolysis" of this bond with formation of the radical (L), which is capable of abstracting hydrogen from the solvent molecule. Examples of oxidative homolysis are well known. [75,76]



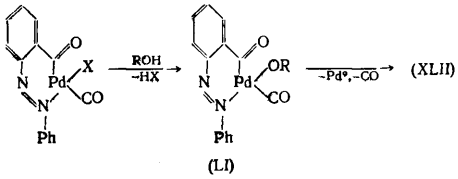
(XLIX)

(L)

The formation of the lactone (XLI), the product of the "double insertion" of CO, can be explained by the repeated palladation of the neighbouring aromatic ring. The key stage in this sequence of reactions is the intramolecular addition of acylpalladium to the carbonyl oxygen of the amide group. The subsequent 1,4-elimination of palladium hydride leads to a lactone (XLI):

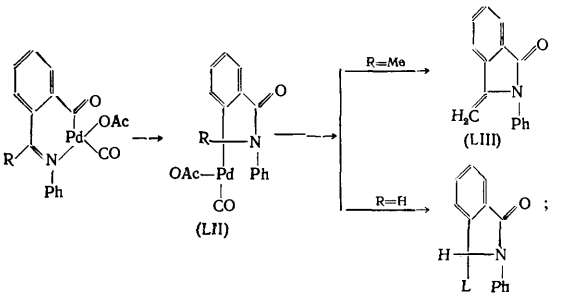


The esters (XLII) are formed as a result of the ethanolysis of compound (XL) [60] or, and we believe this to be more probable, in the course of the reductive decomposition of the complex (LI). We may note that compounds (XL) and (XLII) are also formed in the carbonylation of the analogous azobenzene complexes of platinum(II): [77]



(LI)

2. *Palladated Schiff bases.* The structure of the carbonylation products of these compounds (Table 2, Nos. 5–7) is determined by the presence of the azomethine double bond to which the palladium–acyl group adds. [60] The pathways leading to the further transformation of the σ-derivative (LII) depend on the nature of the substituent R at the C=N double bond and on the presence of an extraneous nucleophile. When R = H, palladium(II) is formally substituted by the nucleophile: by the acetoxy- or carboxy-group, when the reaction is carried out in an inert solvent or in alcohol respectively, and also by the PhNH group when the reaction is carried out in the presence of aniline. When R = Me, the reaction pathway changes and the alkene (LIII) is formed in the course of the 1,3-elimination of palladium:



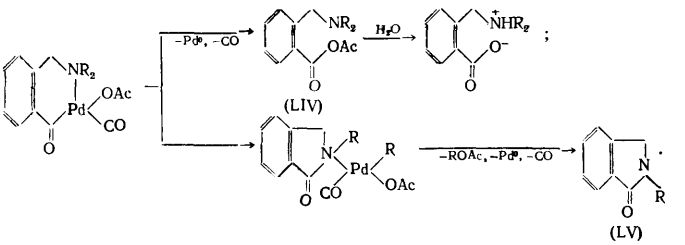
(LII)

(LIII)

L = OAc, OR', NHPh.

The carbonylation of other cyclopalladated complexes containing the N=N and C=N double bonds proceeds analogously to the carbonylation of azobenzene and azomethine derivatives. The principal stages considered above obtain in the reactions of other related complexes and, in conformity with the structure of the final carbonylation products, it is easy to determine the entire sequence of reactions of CO with the given specific palladocycle.

3. *Complexes of NN-dialkylbenzylamines.* Zwitter-ionic products (Table 2, No. 16) are formed in the hydrolysis of the mixed anhydrides (LIV). The formation of the phthalimidine (LV) is accompanied by the dissociation of the N–Me bond. It has been suggested [60] that the nitrogen–carbon bond is ruptured as a result of the 1,2-alkyl shift from nitrogen to palladium. It is of interest that the formation of compound (XXXVI) examined above can involve exactly the same mechanism.

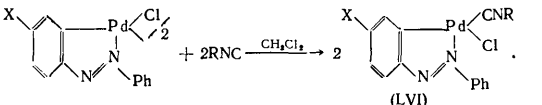


(LIV)

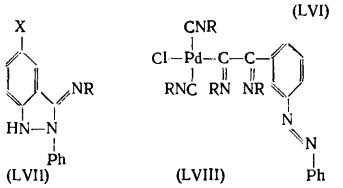
(LV)

VI. REACTIONS WITH ISOCYANIDES AND CARBON DIOXIDE

The reactivity of the isocyanides (CNR) with respect to the transition metal–carbon bond [78] is in many respects analogous to that of carbon monoxide, which is isoelectronic with isocyanides. Under mild conditions, isocyanides, taken in stoichiometric amounts, react [79] with dimeric o-palladised derivatives of azobenzenes, forming the monomeric complexes (LVI):



(LVI)



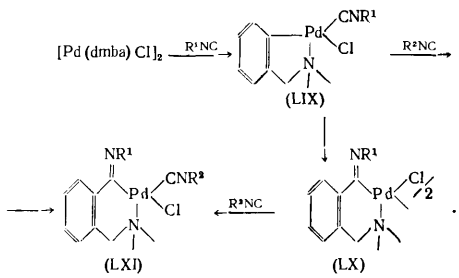
(LVII)

(LVIII)

X = H, OMe; R = Bu-t, C_6H_{11}, C_6H_4Me-o

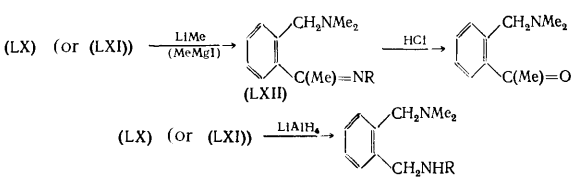
Heating of compounds (LVI) in toluene (at 100–130 °C) leads to 3-imino-2-phenylindazolines (LVII) in 67–90% yields and the process involves the reduction of palladium(II) to zero-valent palladium. The product (LVII) is not formed in the reaction with an excess of *o*-tolyl isocyanide and the complex $[Pd(C_6H_4N{=}NPh)(o\text{-}MeC_6H_4NC)_4Cl]$ is obtained.[79] A similar product has been isolated[80] in the interaction of an excess of cyclohexyl isocyanide with di-μ-chlorobis(azobenzene-C^2,N)dipalladium(II), i.e. $[Pd(azb)Cl]_2$ or $[Pd(C_6H_4N{=}NPh)Cl]_2$. It has been suggested[80] that two molecules of the isocyanide are inserted during the reaction in the Pd–C bond, which results in the formation of compound (LVIII).

The interaction of $[Pd(dmba)Cl]_2$ with isocyanides[81] is presented schematically below:

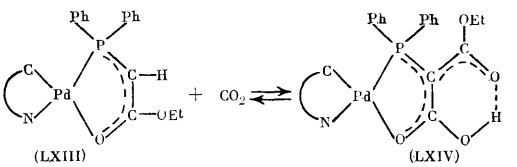


Treatment of the initial complex with a stoichiometric amount of *o*-tolyl isocyanide affords the monomer (LIX). When compound (LIX) is heated in tetrahydrofuran (THF), the coordinated isocyanide is inserted intramolecularly in the Pd–C bond with formation of the iminoacyl complex (LX). The monomer (LIX) can react with an isonitrile of another type with formation of compound (LXI). The ease of insertion of the isocyanides CNR as a function of the nature of the substituent R diminishes in the sequence *o*-tolyl > phenyl > t-butyl. This series shows that the reactivity of the isocyanide is determined by electronic and not steric factors.[81]

The new six-membered iminoacyl palladocycles (LX) and (LXI) are obtained in high yields and this has stimulated their employment as important intermediates for the synthesis of a number of *ortho*-substituted compounds. In particular, the reaction with methyl-lithium or methyl-magnesium iodide leads to the Schiff bases (LXII),[81] whose acid hydrolysis gives rise to the corresponding ketones and reduction with $LiAlH_4$ affords the corresponding diamines:

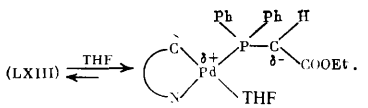


Instances of the insertion of CO_2 in the Pd–C bond in cyclopalladated complexes have not so far been described in the literature. Nevertheless, it is useful to consider one interesting reaction of carbon dioxide. It has been shown recently that the complexes (LXIII) are capable of binding CO_2 reversibly.[82,83] Bubbling of dry CO_2 through their solutions in THF for several seconds leads to the insertion of CO_2 in the PC–H bond and the formation of new complexes of type (LXIV) in which chelation via the oxygen atom of the ester has been replaced by chelation via an oxygen atom of carbon dioxide:



C N = benzyldimethylamine (a) or 8-methylquinoline (b)

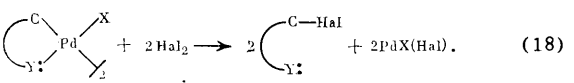
The structure of one of these complexes (LXIVb) has been established by X-ray diffraction.[83] The addition of CO_2 is fully reversible: the initial complex (LXIII) is reformed in a stream of argon and the process can be repeated several times. Despite the fact that the palladocycle is not involved directly in the reaction, in its absence, for example in the case of *cis*-$Pt[Ph_2PCHC(O)OEt]_2$, there is no binding of CO_2. It is believed[83] that the strong *trans*-influence of the σ-linked carbon of the metallocycle has a labilising effect on the Pd–O bond and the carbanionic carbon atom of the reactive 1,3-dipolar form of the complex attacks a carbon dioxide molecule:



VII. HALOGENATION

The reactions of halogens with aromatic hydrocarbons as a rule lead preferentially to *para*-substituted aryl halides.[84] The use of *ortho*-metallated complexes makes it possible to alter radically the halogenation selectivity of and to obtain *ortho*-substituted compounds exclusively.

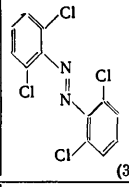
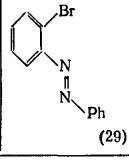
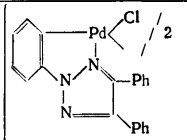
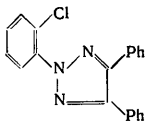
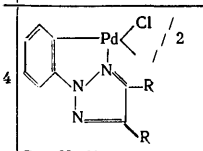
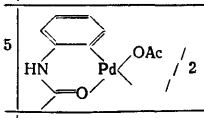
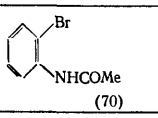
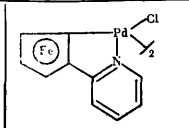
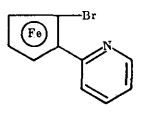
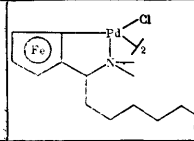
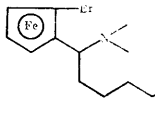
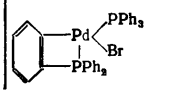
Examples of the action of halogens (Cl_2, Br_2) on cyclopalladated complexes are summarised in Table 3. The reactions proceed in conformity with the equation



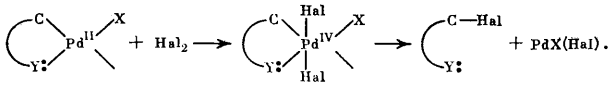
The solvents are aqueous dioxan, methylene chloride, and chloroform. Palladium(II) is not reduced during the reaction. As a result, repeated palladation of the halogenated ligand is possible, which is the cause of the appearance of the 2,6,2′,6′-tetrachloroazobenzene.[85,86] When the reaction time is reduced, 2-chloro-, 2,6-dichloro-, and 2,6,2′-trichloro-azobenzenes are obtained. In contrast to chlorination, polysubstituted products are not formed on bromination.[86]

Only palladium(II) complexes enter into a reaction of type (18). Di-μ-chlorobis(azobenzene-C^2,N)diplatinum(II) is resistant to the action of halogens and the Pt–C bond is not ruptured.[86] In the interaction with halogens of other cyclometallated complexes of platinum group metals, in particular iridium(III) and rhodium(III),[87–89] only the C–H bonds of the metallocycles are chlorinated or brominated, while the M–C bonds remain unchanged. For example, the chlorination of the doubly metallated complex $\{IrCl[P(OC_6H_3Me\text{-}o)_2(OC_6H_4Me\text{-}o)](PEt_3)_2\}$ proceeds with formation of $\{IrCl[P(OC_6Cl_3Me\text{-}o)_2(OC_6H_4Me\text{-}o)](PEt_3)_2\}$.[89]

Table 3. Halogenation of cyclopalladated complexes.

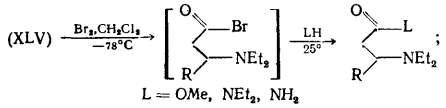
No.	Complex	Halogen	Product (yield, %)	Solvent	Refs.
1	$[Pd(azb)Cl]_2$	Cl_2	 (39)	water–dioxan	[86]
2	То же	Br_2	 (29)	ditto	[86]
3		Cl_2	 (60)	ditto	[129]
4	 R = H, Me	Cl_2	mixture of mono-, di-, and poly-chlorinated products	ditto	[129]
5		Br_2	 (70)	CH_2Cl_2	[36]
6		Br_2	 (35)	$CHCl_3$	[36]
7		Br_2	 (43)	CH_2Cl_2	[29]
8		Br	$\{PdBr_2[PPh_2(C_6H_4Br)]_2\}$, $PdBr_2(PPh_3)_2$	PhH	[91]

The mechanism of the halogenation of palladocycles has not been specially investigated. It may be that the reaction proceeds via the oxidative addition of the halogen to palladium(II) with formation of an octahedral palladium(IV) complex (see, for example, Murenik and Pross[90]), while reductive elimination affords the final products:



The mechanism involving the electrophilic attack by the halogen directly on the palladium–carbon bond might serve as an alternative.

The bromination of acyl derivatives of the palladocycles (XLV) is used to synthesise amides and esters.[68] The intermediate acyl bromides are not isolated; the yield of the final reaction products is quantitative.



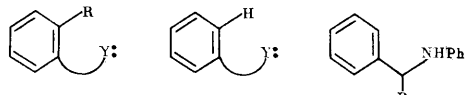
L = OMe, NEt_2, NH_2

Fenton[91] demonstrated the possibility of the chlorination of palladocycles by CCl_4. He obtained the complex $[Pd(o\text{-}ClC_6H_4PPh_2)(PPh_3)Cl_2]$ with an *ortho*-chlorinated ligand from the complex $[Pd(C_6H_4PPh_2)Cl(PPh_3)]$ with a four-membered ring.

Examples of the effective iodination of palladocycles are so far lacking. A report of the possibility of the iodination of dimethylaminomethylferrocene has been reported recently,[92] but the reaction conditions and yields of products are not indicated.

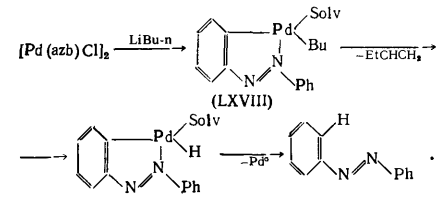
VIII. ALKYLATION, ACYLATION, AND PHOSPHINATION

The *ortho*-alkylated products of the general type (LXV) have been obtained in yields of 22–76% by treating $[Pd(azb)Cl]_2$, $[Pd(dmba)Cl]_2$, and $[Pd(ba)Cl]_2$ with organolithium compounds of the type LiR, where R = Me or Ph, in ether at 0–5 °C.[93,94] The free ligands (LXVI) are formed as side products (up to 38%), while in the case of the benzylideneaniline derivative, compound (LXVII) is formed in addition.



(LXV) (LXVI) (LXVII)

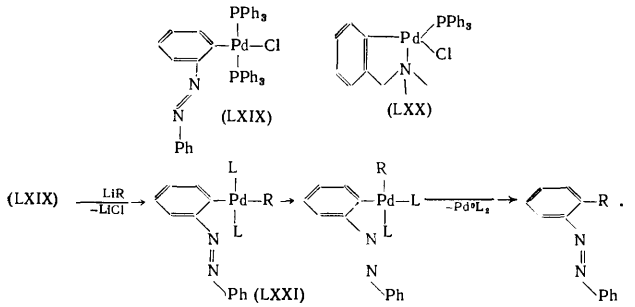
If the group R in the organolithium compound contains β-hydrogen atoms, then the fraction of the reduction products (LXVI) increases significantly. In particular, in the reaction of LiBu-n with $[Pd(azb)Cl]_2$ the yields of compounds (LXV) and (LXVI) are 5 and 89% respectively and in the case of $[Pd(ba)Cl]_2$ the yields of compounds (LXV) and (LXVII) are 1 and 64% respectively. The appearance of reduction products in large amounts when the hydrocarbon group R contains a β-hydrogen atom is associated with the intermediate formation of hydride complexes,[94] whose decomposition leads to compounds (LXVI).



(LXVIII)

In those cases where the group R contains no β-hydrogen atoms, the possibility of the homolysis of the Pd–C bond in the initial complexes has been postulated[94] to account for the formation of compounds (LXVI), although cyclopalladated compounds show no tendency towards spontaneous homolytic decomposition. From our point of view, it is more likely that in this case the homolysis is induced by the groups R

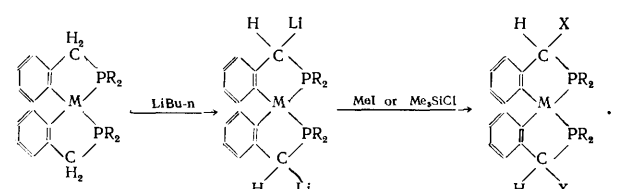
in the intermediate aryl-alkyl or aryl-aryl complex of type (LXVIII). The stability of such compounds increases in the presence of phosphine ligands and it has been found, in conformity with this fact, that the formation of side products in the alkylation of palladocycles is suppressed in the presence of PPh_3; the yields of compound (LXV) increase to 90%.[94] The optimum results are obtained for the ratio $PPh_3 : Pd = 4$. Under these conditions, $[Pd(azb)Cl]_2$ and $[Pd(dmba)Cl]_2$ exist in the forms (LXIX) and (LXX) respectively.[95,96] The mechanism of the alkylation reaction [in relation to compound (LXIX) with $L = PPh_3$] involves the formation of compound (LXXI),[94] its *trans–cis* isomerisation, and reductive elimination:[97,98]



Other phosphorus-containing ligands, for example $P(Bu\text{-}n)_3$, $Ph_2PCH_2CH_2PPh_2$, and $P(OPh)_3$, are less effective as inhibitors of side processes than PPh_3. Apart from organolithium compounds, the Grignard reagents MeMgBr, PhMgBr, and $H_2C = CHMgBr$ have been used. In the last case *o*-substituted arylolefins, analogous to those obtained in the reactions of palladocycles with alkenes (see Section III), are formed.[94]

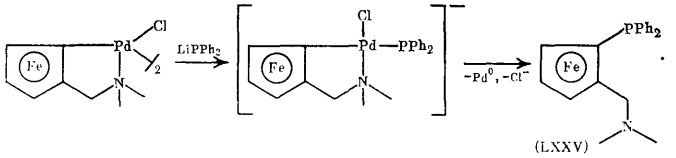
The alkylation of $[Pd(ba)Cl]_2$ by secondary organolithium compounds leads to compounds (LXV) in low yields even in the presence of PPh_3 and is accompanied by the secondary–normal isomerisation of the alkyl group.[99] We may note that the "double" alkylation of $[Pd(ba)Cl]_2$, i.e. the repeated palladation of compound (LXV) and treatment with LiR followed by the acid hydrolysis of the reaction products, leads to 2,6-disubstituted aromatic aldehydes which are difficult to obtain by other methods.[94] Treatment of palladised 2-pyridylferrocene in benzene with LiBu-n and LiPh afforded o-substituted products in yields of 34 and 27% respectively.[66] The alkylation of the iminoacyl complexes (LX) and (LXI) was considered above.

The interaction of n-butyl-lithium with the complexes (LXXII) proceeds via a different pathway.[100] The M–C bond is not then involved, the methylene groups of the complexes being substituted by lithium. Treatment of compound (LXIII) with methyl iodide or trimethylsilyl chloride results in the modification of the cyclometallated ligands in the complexes (LXXIV):



M = Pd, Pt; R = Me, Ph;
X = Me, Me_3Si

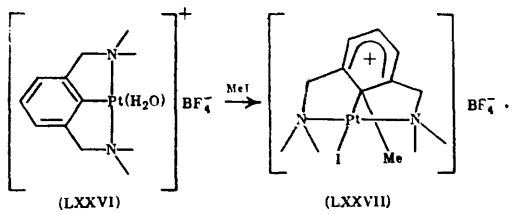
The phosphination of palladocycles is on the whole carried out analogously to alkylation, but in this case the complex is treated with $LiPPh_2$.[101] If the initial cyclopalladation of the substituted ferrocene is carried out asymmetrically, then the enantiomeric ligand (LXXV) with planar chirality is formed:



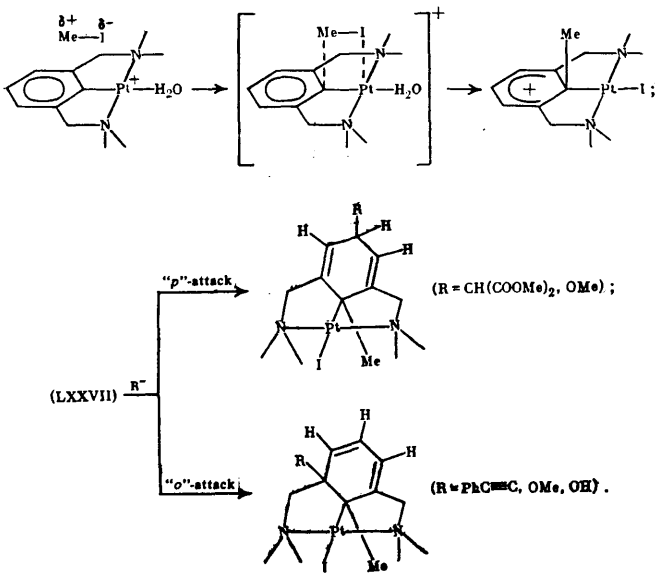
Such ligands have found extensive applications, particularly in the asymmetric cross-coupling reactions of Grignard reagents and organic halogeno-derivatives catalysed by palladium and nickel complexes.[102,103] The highest stereoselectivity is ensured when the ligands L contain elements of planar chirality.[103]

$$R{-}\underset{\underset{Me}{|}}{CH}{-}MgBr + R'Br \xrightarrow{LM} R{-}\underset{\underset{Me}{|}}{CH}{-}R' + MgBr_2 .$$

Direct alkylation of cyclometallated complexes by alkyl halide is so far known for platinum(II) complexes.[104] The reaction of compound (LXXVI) with an excess of methyl iodide in acetone leads to the unusual product (LXVII) whose structure has been established by X-ray diffraction. The central atom of the complex had a slightly distorted square-planar configuration, while the aryl ligand has the boat form.

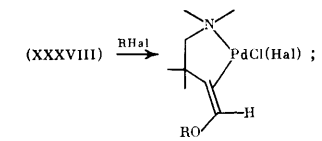


The addition of MeI is reversible: in the presence of NaX (X = Cl, Br, or I) the product is $\{PtX[C_6H_3(CH_2NMe_2)_2\text{-}oo']\}$ in aqueous solutions, while the initial complex (LXXVI) is regenerated in boiling water or aqueous acetone solution. An excess of NaCN decomposes the complex (LXXVII) with formation of $oo'\text{-}(Me_2NCH_2)_2C_6H_3Me$.[105] It is most likely that the mechanism of the formation of compound (LXXVII) involves the direct addition of methyl iodide to compound (LXXVI):[104]



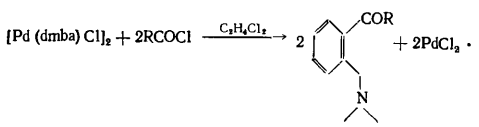
The cationic complex (LXXVII) gives rise to *para*- and *ortho*-addition products on reaction with the strong bases $CH(COOMe)_2^-$, $PhC\equiv C^-$, MeO^-, and HO^-.[105] Depending on the reaction conditions, the "*para*"- or "*ortho*"-attack may be made to predominate. Treatment of these complexes with powerful non-coordinating acids (except for $R = PhC_2^-$) leads to a high yield of the initial compound (LXXVII).

In the interaction of compound (XXXVIII) with allyl bromide and benzyl chloride the hydrocarbon fragment attacks the carbonyl oxygen atom of the complex, which results in the formation of a complex without a palladium–carbon σ-bond:[54]

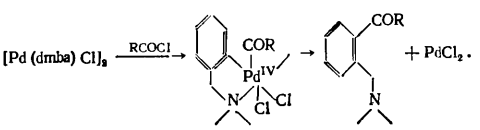


$R = CH_2CH{=}CH_2, CH_2Ph$; Hal = Cl, Br.

The acylation of dimers of type $[Pd(dmba)Cl]_2$ leads to aryl ketones:[106]



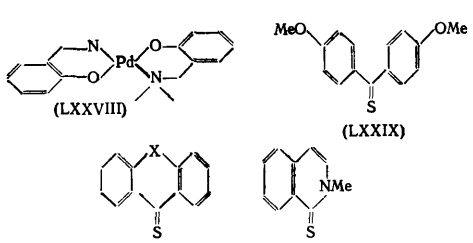
On the one hand, acyl and benzoyl chlorides and, on the other, unsubstituted *ortho*-palladised *NN*-dialkylbenzylamines as well as their analogues with electron-donating substituents enter into the reaction. The yields of aryl ketones are 25–93%. Palladocycles with a chlorine atom in the ring are unreactive. The acylation mechanism[106] involves oxidative addition with the intermediate formation of palladium(IV) and the subsequent reductive elimination of palladium(II) chloride:

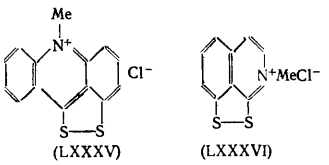


The interaction of palladocycles with acyl halides has also been described by Clark et al.[107]

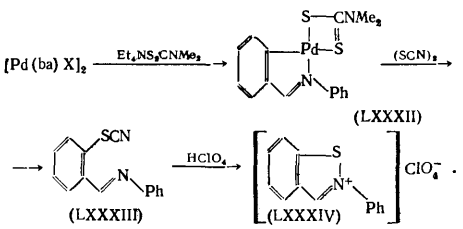
IX. OTHER REACTIONS

The anodic oxidation of $[Pd(azb)OAc]_2$ and $[Pd(dmba)OAc]_2$ does not result in the formation of any isolatable organic products.[108] On the other hand, the oxidation of $[Pd(dmba)Cl]_2$ with *m*-chloroperbenzoic acid in methylene chloride at 0 °C followed by treatment with $NaBH_4$ in methanol leads to a palladium(II) complex of salicylaldimine (LXXVIII) in 35% yield.[109]





Cyclopalladation is a key stage in the syntheses of derivatives of isothiazoles and 1,2-dithiols[110] from metallated benzylideneaniline, 2-pyridylbenzene, benzo[*h*]-quinoline, and the sulphur-containing arenes (LXXIX)–(LXXXI). The pathway leading to isothiazoles is illustrated below using as an example the reaction of palladised benzylideneaniline. The initial complexes are treated with tetraethylammonium *NN*-dialkyldithiocarbamate, which converts them into the monomers (LXXXII):



On treatment with thiocyanogen in chloroform, the latter give rise to the thiocyanates (LXXXIII) and the very sparingly soluble complex $[Pd(Me_2NCSS)SCN]_2$. Compounds (LXXXIII) are stable only in the case of 2-pyridylbenzene and benzo[*h*]quinoline, but treatment of even unstable intermediates with perchloric acid leads to isothiazoles of type (LXXXIV). In the case of compounds (LXXXb) and (LXXXI) best results are achieved when the analogues (LXXXII) react with *N*-sulphenylmorpholine chloride, which results in the formation of the 1,2-dithiols (LXXXV) and (LXXXVI). The yields of isothiazoles and 1,2-dithiols are 25–90 and 81–91% respectively.

A pathway to *ortho*-deuteriated aromatic ketones has been proposed by Alper.[111] Refluxing of the *ortho*-palladated compounds (LXXIX) and $O=C(C_6H_4Me\text{-}p)_2$ in MeOD for 18 h leads to $O=C(C_6H_4X\text{-}p)(C_6H_4D\text{-}o\text{-}X\text{-}p)$, where X = OMe or Me, in yields of 82 and 84% respectively. The transamination of complexes of Schiff bases has been described.[112]

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The reactions considered indicate the extensive possibilities of the application of cyclopalladated compounds and also the related complexes of other transition metals in organic sythesis. Their use is of greatest interest in the preparation of organic compounds which are difficult to obtain by other procedures and also of enantiomeric and diastereoisomeric molecules. Bearing in mind that chiral palladocycles are also used for the separation of racemates, for example, those of tertiary phosphines,[113,114] one may hope that this field of chemistry, which is developing at the frontier between organic and organometallic chemistry as well as metal complex catalysis, will undergo further natural development.

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Metal Complex Catalysts for the Hydrogenation of Aromatic and Heterocyclic Compounds

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The application of metal complex catalysts (in homogeneous and heterogenised forms) to the hydrogenation of aromatic and heterocyclic compounds is examined.
The bibliography includes 128 references.

CONTENTS

I. Introduction 171
II. Catalysts for the hydrogenation of aromatic hydrocarbons 171
III. Hydrogenation of heterocyclic compounds 180

I. INTRODUCTION

The study of the hydrogenation of aromatic and heterocyclic compounds constitutes an important (from both practical and theoretical standpoint) and at the same time a complex problem. There are numerous literature data on the hydrogenation of the above compounds (see, for example, Smith,[1] Bel'skii and Shostakovskii,[2] Kreile et al.,[3] and Mashkina[4]), but these concern mainly only heterogeneous-catalytic reactions, requiring as a rule the use of fairly severe conditions, which entails in its turn a decrease in the selectivity of the processes.

A much smaller number of studies have been devoted to the hydrogenation of aromatic and heterocyclic compounds in the presence of metal complex catalysts apparently owing to the difficulty of selecting metal complexes capable of activating aromatic and heterocyclic compounds and at the same time remaining resistant to the poisoning activity of the latter. Nevertheless the synthesis and employment of metal complexes as hydrogenation catalysts (homogeneous and particularly heterogenised catalysts which possess simultaneously the advantages of homogeneous and traditional heterogeneous catalysts) is extremely promising, since it permits the process to be carried out under mild conditions, which significantly increases the yield of products and the reaction selectivity.

The advantages and disadvantages of metallic and metal complex catalysts combined with the theoretical development of a general approach to the investigation of the characteristic features of catalytic reactions of organic compounds in the presence of these systems in the course of various processes (deuterium–hydrogen exchange, hydrogenation, oxidation, etc.) have been considered in a number of publications (see, for example, Refs.5–17).

Hydrogenation is one of the first reactions carried out using metal complex catalysts. A number of reviews have been devoted to this question (for example, those of James,[18] Coffy,[19] and McQuillin,[20] in which mainly the hydrogenation of compounds containing bonds of the olefinic type is discussed. This review deals with the available literature data for the hydrogenation of aromatic and heterocyclic compounds in the presence of metal complex catalysts—both homogeneous and heterogenised. Instances of the hydrogenation of unsaturated substituents are excluded from consideration if such hydrogenation does not entail the hydrogenation of the aromatic or heterocyclic ring.

II. CATALYSTS FOR THE HYDROGENATION OF AROMATIC HYDROCARBONS

1. Catalysts Active under Hydroformylation Conditions

Dicobalt octacarbonyl was the first metal complex catalyst used for the hydrogenation of aromatic and heterocyclic compounds.[21] However, its use requires the reaction to be carried out in the presence of an excess carbon monoxide pressure and hydrocarbonylation can therefore occur to a greater or lesser extent together with the hydrogenation reaction.

Benzene and its alkyl-derivatives are hardly hydrogenated under hydroformylation conditions.[22,23] For example, only a slight degree of conversion of benzene into hydroxymethylcyclohexane has been noted[22] to occur at 200 °C and an initial pressure of the $CO : H_2 = 1 : 1$ mixture of 300 atm.†

Hydrogenation under hydroformylation conditions has been studied in greatest detail for condensed polycyclic aromatic hydrocarbons[21,23–26] (Table 1). Overall, the hydrogenation of polycyclic aromatic hydrocarbons proceeds more readily than the hydrogenation of benzene and the rings condensed with two or several other aromatic rings are mainly hydrogenated. Thus anthracene is readily converted into 9,10-dihydroanthracene (Table 1).

The low activity of dicobalt octacarbonyl in the hydrogenation of naphthalene and phenanthrene should also be noted. In addition, the naphthalene and phenanthrene system formed in the hydrogenation of polynuclear aromatic compounds are as a rule fairly resistant to further reduction[23] (Table 1).

The absence of stereoselectivity in the hydrogenation reactions under hydroformylation conditions has been demonstrated for 9,10-dimethylanthracene;[24] *cis*- and *trans*-9,10-dihydro-9,10-dimethylanthracenes are formed in approximately equal amounts. The addition of tributyl phosphite does not increase the selectivity but lowers the activity of the catalyst and *cis–trans* isomerisation is not observed.

The deuteriation of polycyclic aromatic compounds in the presence of the $D_2 : CO = 1 : 1$ mixture at approximately

† Here and henceforth the initial pressure at room temperature before heating the reaction mixture is quoted.

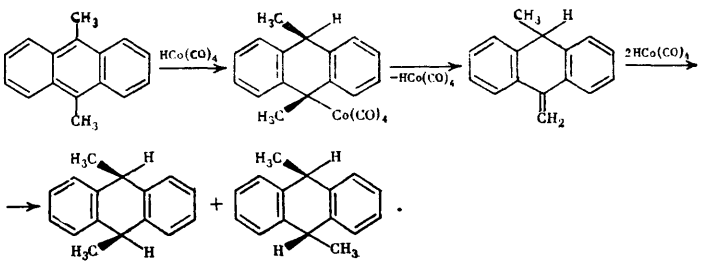
200 °C, which is catalysed by $Co_2(CO)_8$, has been investigated.[27] Anthracene and anthraquinone are converted into 9,9,10,10-tetradeuterio-9,10-dihydroanthracene, pyrene undergoes reduction and H–C exchange in the 4- and 5-positions, while phenanthrene does not react.

Table 1. Hydrogenation of condensed polycyclic aromatic hydrocarbons under hydroformylation conditions*.

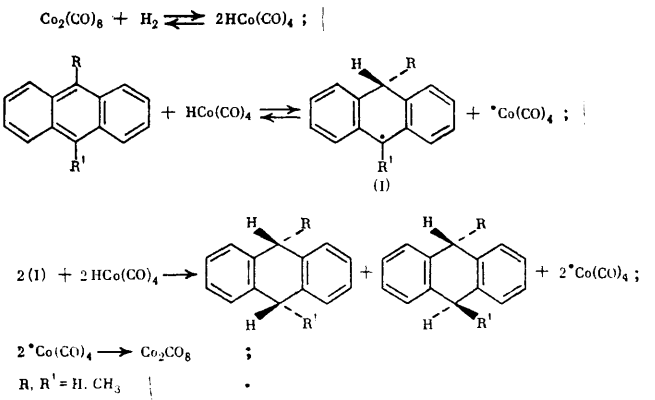
Substrate	Hydrogenation products (yield, %)
Phenanthrene**	9,10-Dihydrophenanthrene (7); 1,2,3,4-tetrahydrophenanthrene (1)
Naphthalene	Tetralin (16)
2-Methylnaphthalene	Methyltetralins (43)
1,1-Binaphthyl	Is not hydrogenated
Acenaphthene	2a,3,4,5-Tetrahydroacenaphthene (45)
Fluorene	Is not hydrogenated
Anthracene	9,10-Dihydroanthracene (99)
Naphthacene	5,12-Dihydronaphthacene (70)
Chrysene	5,6-Dihydrochrysene (24)
Fluoranthrene	1,2,3,10c-Tetrahydrofluoranthrene (54)
Triphenylene	Is not hydrogenated
Pyrene	4,5-Dihydropyrene (69)
Perylene	1,2,3,10,11,12-Hexahydraperylene (72)
Coronene	Is not hydrogenated

*Catalyst—dicobalt octacarbonyl, 1–5 mole %, 150–200 °C, 200 atm pressure of $H_2 : CO = 1 : 1$ mixture (2 : 1 in the case of phenanthrene).
**According to the results of Wender et al.;[21] in the remaining cases the data of Freedman et al.[23] were used.

In order to establish the mechanism of the hydrogenation reaction, a study has also been made of the reduction of anthracene and 9,10-dimethylanthracene by the stoichiometric amount of $HCo(CO)_4$.[24] It has been shown that anthracene is hydrogenated to 9,10-dihydroanthracene to the extent of 25% at 25 °C, while 9,10-dimethylanthracene is 99% hydrogenated with formation of 35% of the *cis*-isomer and 65% of the *trans*-isomer of 9,10-dihydro-9,10-dimethylanthracene. The following reaction mechanism, which explains the formation of the *cis*- and *trans*-products, has been put forward:



At the same time, it is believed[28] that organometallic intermediates are not formed in the hydroformylation of polycyclic aromatic compounds. This conclusion is based on the analysis of data for the deuteriation of anthracene and pyrene under deuterioformylation conditions[27] as well as the following facts: (1) the absence of hydroxymethylation products from the reaction mixture after the hydrogenation of polycyclic aromatic compounds under hydroformylation conditions and (2) the easier hydrogenation of 2-methylnaphthalene or acenaphthene compared with naphthalene[23] and of 9,10-dimethylanthracene compared with anthracene[24] despite the steric hindrance. A radical reaction mechanism has therefore been put forward:[28]



2. Catalysts of the Ziegler Type

A number of studies on the hydrogenation of aromatic hydrocarbons in the presence of Ziegler catalysts have been described in the literature.[31–41] It is noteworthy that data[29] concerning the catalytic activity of a number of transition metal salts in the course of the hydrogenation of aromatic compounds have been refuted in another study.[30] The addition of aluminium alkyls or aluminium hydrides to the reaction mixture containing transition metal ions increases sharply the activity of the catalyst. Overall, catalysts of the Ziegler type make it possible to carry out the hydrogenation under much milder conditions than in the presence of $Co_2(CO)_8$. Thus the addition of aluminium alkyls or aluminium hydrides to cobalt and nickel carboxylates makes it possible to obtain catalysts for the hydrogenation of benzene which are active at temperatures of approximately 50 °C and pressures of approximately 30 atm.[31]

The hydrogenation of benzene under mild conditions (30 °C, 2 atm) has been studied using the triethylaluminium–cobalt acetylacetonate system.[32] On the basis of EPR studies, it has been suggested that the zerovalent cobalt complex decomposes with formation of clusters which directly propagate the hydrogenation reaction.

The reduction of iron, cobalt, and nickel acetylacetonates with sodium and lithium tetrahydroborates and lithium tetrahydroaluminate makes it possible to obtain benzene hydrogenation catalysts which are active at 30 °C and 1 atm.[33] Catalysts for the hydrogenation of benzene, toluene, and xylene have been obtained by the reduction of cobalt, nickel, and copper complexes of salicylaldehyde with $LiAlH_4$ using metal : aluminium ratios ranging from 1 : 1 to 1 : 7.[34]

The addition of triethylaluminium to transition metal 2-ethylhexanoates or naphthenates yields active catalysts for the hydrogenation of aromatic compounds.[35,36] The catalysts are prepared in solvents which show no tendency towards complex formation, such as heptane, benzene, etc.; this is accompanied by the evolution of a gas containing 95% of ethane. The maximum catalytic activity in the case of nickel is attained for the Al : Si = 3 : 1–4 : 1 ratios. The activity in the hydrogenation of benzene diminishes in the sequence Ni ≥ Co > Fe > Cr > Cu. In mixtures containing 0.3–0.5 mole % of nickel 2-ethylhexanoate for an initial hydrogen pressure of approximately 70 atm and temperatures in the range 150–200 °C, fairly rapid and quantitative reduction of benzene to cyclohexane, of phenol to cyclohexanol, and of dimethyl phthalate to dimethyl hexahydrophthalate takes place. The hydrogenation of pyridine to piperidine, of

dimethyl terephthalate to dimethyl hexahydroterephthalate, and of naphthalene to tetralin and decalin proceeds less actively.[35]

The stereoselectivity of the hydrogenation reaction in the presence of a system containing nickel has been pointed out.[37] o-Xylene has been hydrogenated to 66% of *cis*-1,2-dimethylcyclohexane and 34% of *trans*-1,2-dimethylcyclohexane. It has been possible to hydrogenate polystyrene to a product with a 15% content of cyclohexane rings by weight at 150 °C and an H_2 pressure of 100 atm. Physicochemical investigation has demonstrated that the nickel in the catalyst is reduced to the zerovalent diamagnetic state.[37]

Table 2. Hydrogenation of aromatic hydrocarbons in the presence of the cobalt 2-ethylhexanoate/$AlEt_3$ catalyst.[38]

Substrate	a *	Al:Co	τ, h	α **, %	Products (composition, %)
Benzene	0.25	2	30	63	Cyclohexane (100)
o-Xylene	0.2	2	15	50	1,2-Dimethylcyclohexane (*cis*-70, *trans*-26)
m-Xylene	0.2	2	22	40	1,3-Dimethylcyclohexane (*cis*-63, *trans*-37)
p-Xylene	0.1	2	24	55	1,4-Dimethylcyclohexane (*cis*-63, *trans*-37)
Biphenyl	0.05	2	20	100	Bicyclohexyl (81); phenylcyclohexane (19)
Naphthalene	0.05	2	18	100	Decalin (*cis*-43, *trans*-11), tetralin (37)
Tetralin	0.1	2	66	100	Decalin (*cis*-66, *trans*-34)

*Substrate: catalyst molar ratio.
**Degree of conversion.

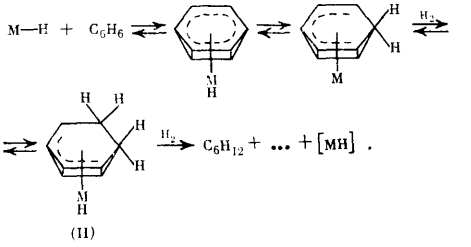
The analogous system based on cobalt 2-ethylhexanoate has been investigated[38] (Table 2). The hydrogenation was carried out at 20–30 °C at a hydrogen pressure of 65 atm. In addition a study has been made of the hydrogenation of a number of polar compounds at an initial hydrogen pressure of 50–60 atm. Phenol is 25% hydrogenated at 45 °C in the course of 20 h to give a mixture of 98% of cyclohexanol and 2% of cyclohexanone. Diethyl phthalate has been 95% hydrogenated at 20 °C during 16 h and the products were found to contain 83% of diethyl *cis*-hexahydrophthalate and 17% of the *trans*-isomer. The same workers[38] showed in a study of competitive hydrogenation that olefins and naphthalene prevent the hydrogenation of benzene.

The hydrogenation of benzene and its alkyl derivatives in the presence of acetylacetonate, cyclopentadienyl, and dimethylglyoximate complexes reduced with trialkylaluminium has been studied.[39,40] The relative activities of different complexes in the benzene hydrogenation reaction[40] vary in the following sequence:

$$Ni(C_5H_7O_2)_2 > Co(C_5H_7O_2)_2 \geqslant Cu(C_5H_7N_2O_2)_2 > Fe(C_5H_7O_2)_3 > Fe(C_5H_5)_2 > > Mn(C_5H_7O_2)_2 > VO(C_5H_7O_2)_2 > Ni(C_5H_7N_2O_2)_2 > (C_5H_5)_2TiCl_2 > Cr(C_6H_7O_2)_3 .$$

Here C_5H_5 = cyclopentadienyl, $C_5H_7O_2$ = acetylacetonate, and $C_5H_7N_2O_2$ = dimethyl glyoximate. The apparent activation energy for the hydrogenation of benzene in the presence of iron and nickel acetylacetonates does not vary with the Al : metal ratio; consequently the number of active complexes and not the "energy relations" of the process vary. The experimental activation energy for the hydrogenation of benzene in the presence of acetylacetonate complexes diminishes in the sequence[41] Cu > Ni > Fe > Cr > Mo when the Al : metal ratio is 8 : 1 for Cr, Fe, and Ni and 6 : 1 for Cu and Mo. In the hydrogenation of benzene, toluene, *o*-xylene, and mesitylene in the presence of nickel and iron acetylacetonates the activation energy diminishes with increase of the number of alkyl substituents, while in the presence of chromium and molybdenum acetylacetonates it increases.[41]

At 150 °C in the presence of nickel acetylacetonate the hydrogenation reaction is of first order with respect to hydrogen, while the order with respect to benzene varies from a fraction less than unity to zero; in the presence of chromium acetylacetonate the reaction order with respect to hydrogen is less than unity.[41] On the basis of their results, the authors[39] proposed the following mechanism for the benzene hydrogenation reaction assuming that the metal hydride is the active catalytic species:



(II)

It has been suggested that the rate-limiting stage is the activation of the hydrogen molecule involving the formation of the hydride (II).

3. Metal Complexes Containing Unsaturated and Aromatic Hydrocarbons as Ligands

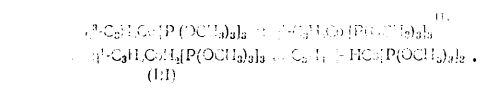
A large number of studies have been devoted to the hydrogenation of aromatic hydrocarbons in the presence of complexes containing unsaturated hydrocarbons as ligands.

The catalytic activity of pentamethylcyclopentadienyl complexes has been investigated in the hydrogenation of olefins and aromatic hydrocarbons.[42–45] Di-μ-chlorobis[chloro(pentamethylcyclopentadienyl)rhodium] $[Rh(\eta^5\text{-}C_5Me_5)Cl_2]_2$ is an active catalyst of the hydrogenation of aromatic hydrocarbons; its iridium analogue is much less active. A heterolytic mechanism has been proposed for the activation of hydrogen, since the catalyst is active in the presence of 15 moles of NEt_3 per mole of the catalyst. The base is required to bind the HCl evolved in the activation of H_2 and to promote the formation of rhodium hydride.[44] The intermediate formation of partial reduction products has not been observed in the hydrogenation of benzene.

Table 3 presents the results of the hydrogenation of a number of aromatic compounds in the presence of $[Rh(\eta^5\text{-}C_5Me_5)Cl_2]_2$ at 50 °C and a hydrogen pressure of 50 atm. A fairly high stereoselectivity has been noted in the hydrogenation of xylenes. The ratio of the *cis*- and *trans*-isomers in the hydrogenation products is 6.2 : 1.0 for *o*-xylene, 3.8 : 1.0 for *m*-xylene, and 2.0 : 1.0 for *p*-xylene. An increase in the number of alkyl substituents hinders the hydrogenation of the aromatic ring. In terms of the relative rates of hydrogenation alkylbenzenes can be arranged in the following sequence:[45] benzene (1.00) > toluene (0.94) > *o*-xylene (0.70) > ethylbenzene (0.58) > mesitylene (0.35) > s-butylbenzene (0.25) > durene (0).

Extensive studies have been carried out on the hydrogenation of various aromatic compounds in the presence of $\eta^3\text{-}C_3H_5Co[P(OCH_3)_3]_3$ and related catalysts.[46–53] The possibility of the hydrogenation of benzene under mild conditions has been demonstrated: 25 °C, p_{H_2} = 1 atm, $\eta^3\text{-}C_3H_5Co$.

.$[P(OCH_3)_3]_3$ catalyst.[47] The complex is stable in approximately 20 benzene hydrogenation cycles and then decomposes into inactive species. Even at low partial hydrogen pressures and in the initial stages of the reaction, partially hydrogenated benzenes were not detected. During 24 h from the start of the reaction, a visible decomposition of the complex, accompanied by the breakdown of homogeneity, is not observed. On decomposition of the complex, phosphite and $HCo[P(OCH_3)_3]_4$ are detected in solution. It has been suggested[48] that the π-allyl ligand is eliminated when the complex decomposes:

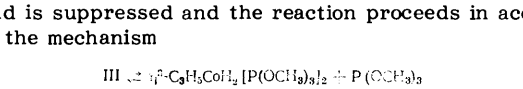


(III)

Table 3. Hydrogenation of aromatic compounds in the presence of the di-μ-chlorobis[chloro(pentamethylcyclopentadienyl)rhodium] catalyst.[44]

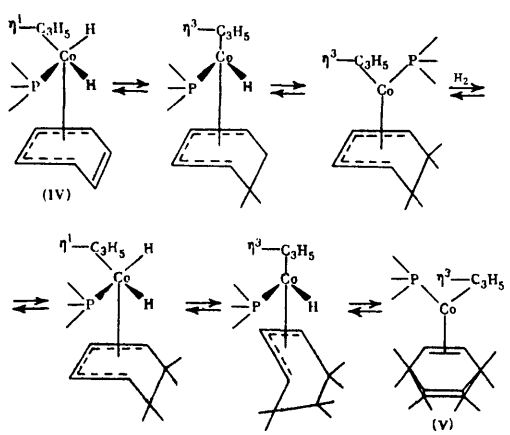
Substrate	Reaction products (yield, %)
Styrene	Ethylbenzene (97); ethylcyclohexane (3)
Phenylacetylene	Styrene (7)
Anisole	Methoxycyclohexene (19); methylcyclohexane (6)
Phenol	Cyclohexanone (1); cyclohexene (0.5)
Methyl benzoate	Methyl cyclohexanoate (75); toluene (8)
Acetophenone	Cyclohexyl methyl ketone (100)
Benzophenone	Dicyclohexyl ketone (50); cyclohexyl phenyl ketone (15); dicyclohexylmethanol (10)
NN'-Dimethylaniline	*NN*'-Dimethylcyclohexylamine (73)
Nitrobenzene	Aniline (96); cyclohexane (4)
Fluorobenzene	Fluorocyclohexane (14); cyclohexane (38)
Bromobenzene	Cyclohexane (10)
Iodobenzene	Cyclohexane (2); benzene (3)
Anthracene	Tetrahydroanthracene (70); octahydroanthracene (22), perhydroanthracene (3)

In the presence of an arene, the *cis*-elimination of the ligand is suppressed and the reaction proceeds in accordance with the mechanism

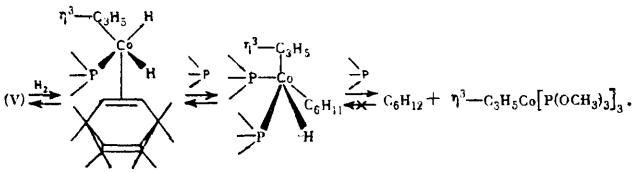


(IV)

Benzene is hydrogenated in the intermediate complex (IV) in accordance with the mechanism:[48]



(V)



The above scheme accounts for the absence of the products of the partial reduction of the aromatic benzene ring from the reaction mixture and for the high *cis*-stereoselectivity of the hydrogenation of substituted benzene derivatives. It has been noted[48] that the rate of hydrogenation of benzene is much higher than that of cyclohexene.

Table 4. Hydrogenation of aromatic compounds in the presence of η^3-$C_3H_5Co[P(OCH_3)_3]_3$.* [49]

Substrate	a**	τ, h	Reaction products (yield, %)
Benzene	1:100	24	Cyclohexane (16)
Benzene	1:100	24	Cyclohexane (16.4)
Benzene	1:100	10	Cyclohexane (5)
Benzene + D_2	1:100	10	*cis*-$C_6H_6D_6$ (5)
Perdeuteriobenzene	1:100	15	*cis*-$C_6H_6D_6$ (8)
Toluene	1:100	10	Methylcyclohexane (5)
o-Xylene	1:100	10	*cis*-1,2-Dimethylcyclohexane (3)
o-Xylene	1:100	48	*cis*-1,2-Dimethylcyclohexane (15)
m-Xylene	1:100	10	*cis*-1,3-Dimethylcyclohexane (3)
m-Xylene	1:100	48	*cis*-1,3-Dimethylcyclohexane (7)
p-Xylene	1:100	10	*cis*-1,4-Dimethylcyclohexane (3)
p-Xylene	1:100	49	*cis*-1,4-Dimethylcyclohexane (7)
Mesitylene	1:100	15	*cis,cis*-1,3,5-Trimethylcyclohexane (1)
1,2,3-Trimethylbenzene	1:10	65	*cis,cis*-1,2,3-Trimethylcyclohexane (2)
1,2,4,5-Tetramethylbenzene	1:10	72	*cis,cis,cis*-1,2,4,5-Tetramethylcyclohexane (9)
Naphthalene	1:10	168	*cis*-Decalin (99); tetralin (1)
Anthracene	1:10	40	*cis,syn,cis*-Perhydroanthracene (76); mixture of products (14)
Furan	1:100	15	Tetrahydrofuran (14)
Benzofuran	1:100	96	Perhydrobenzofuran (19); C_8H_8O (12); $C_8H_{12}O$ (1.5)
Anisole	1:100	10	Cyclohexyl methyl ether (5)
NN'-Dimethylaniline	1:100	48	*NN*'-Dimethylcyclohexylamine (3)
Ethyl benzoate	1:13	24	Ethyl cyclohexanecarboxylate (2); ethyl cyclohex-1-enecarboxylate (13)
NN'-Dimethylbenzamide	1:10	68	*NN*'-Dimethylcyclohexanecarboxamine (54); benzyl alcohol (4)
Acetophenone	1:50	24	Cyclohexyl methyl ketone (1)
Cyclohex-2-en-1-one	1:47	42	Cyclohexanone (3)
Styrene	1:41	24	Vinylcyclohexane (5); ethylbenzene (6); ethylcyclohexane (4)
1-Phenylpropyne	1:23	43	Propenylcyclohexane (2); propylbenzene (3); allylbenzene (1); *cis*-propenylbenzene (1); *trans*-propenylbenzene (1)
Propylbenzene	1:34	25	Propylcyclohexane (15)
Allylbenzene	1:36	30	Allylcyclohexane (2); propylcyclohexane (3); propylcyclohexene (5); propylbenzene (4)
Cyclo-octa-1,5-diene	1:32	37	Cyclo-octene (50); cyclo-octane (26)

*Reaction conditions: 20 °C, 1 atm H_2, 0.112 mmol of catalyst.

**Catalyst : substrate molar ratio.

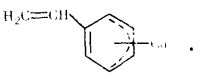
The results of the study of hydrogenation in the presence of η^3-$C_3H_5Co[P(OCH_3)_3]_3$ have been surveyed[49] (Table 4). In the presence of this system, polycyclic hydrocarbons are hydrogenated less effectively than benzene. Electron-accepting substituents deactivate the aromatic ring: fluorobenzene and nitrobenzene were not hydrogenated, since the reaction requires a high π-donor capacity of the aromatic ring. Nucleophilic substituents are in their turn bound preferentially to the metal atom, preventing the hydrogenation of the aromatic ring, as happens, for example, in the case of phenylacetonitrile, triphenylphosphine, and benzonitrile. The oxidation-reduction interaction of the catalyst with

chlorobenzene prevents the hydrogenation of the latter. Protonation of the catalyst leads to the unstable complex η^3-$C_3H_5CoH[P(OCH_3)_3]_3^+$, which decomposes with evolution of propene. For this reason, it has not been possible to hydrogenate phenol and benzoic acid.

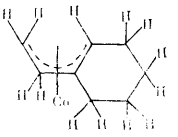
The influence of steric hindrance following the introduction of alkyl substituents into the benzene ring and the consequent resistance of 1,2,3,4-tetramethylbenzene and hexamethylbenzene to hydrogenation have been noted.[49]

When the competitive hydrogenation of a mixture of benzene and hex-1-ene is carried out,[49] the ratio of the hydrogenated aromatic hydrocarbon and hexane is 7 : 10 and appreciable amounts of cyclohexene are formed. Thus alkenes are bound to the catalyst less strongly than aromatic hydrocarbons and the alkene which has failed to react can competitively displace the products of the partial reduction of aromatic hydrocarbons.

The hydrogenation of styrene leads to the formation of approximately equal amounts of vinylcyclohexane, ethylbenzene, and ethylcyclohexene for a low degree of conversion. This composition of the reaction products can be accounted for by the competitive displacement of the partly hydrogenated products. On the other hand, there is a possibility (by virture of steric factors) of the following type of interaction with the catalyst:



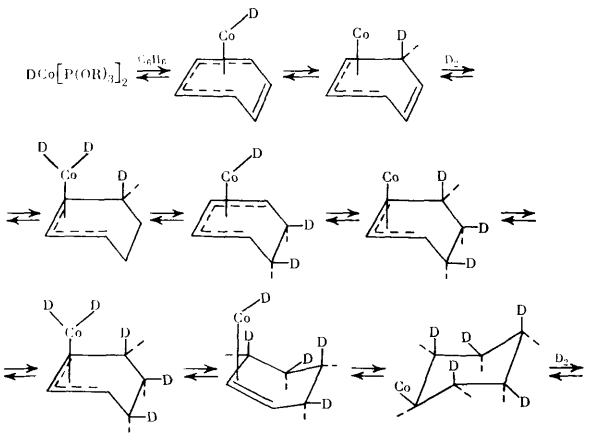
After the addition of four hydrogen atoms, the intermediate

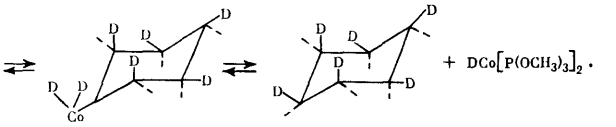


is formed and, after combining with a further two hydrogen atoms, the latter can give rise to vinylcyclohexane and cyclohexenylethane.

Experiments on the deuteriation of benzene using perdeuteriobenzene[49] demonstrated the absence of H–D exchange involving the aromatic ring; thus the hydrogen addition stage is irreversible. The absence of deuterium from the propene evolved after the decomposition of the complex indicates the irreversibility of the decomposition of the latter. Deuteriation of benzene and hydrogenation of C_6D_6 lead to the formation of *cis*-stereoisomers. The deuteriation of the side chain in alkylbenzenes has also been observed.[49,50]

A mechanism has been proposed for the *cis*-deuteriation reaction:[51]

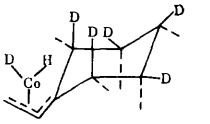




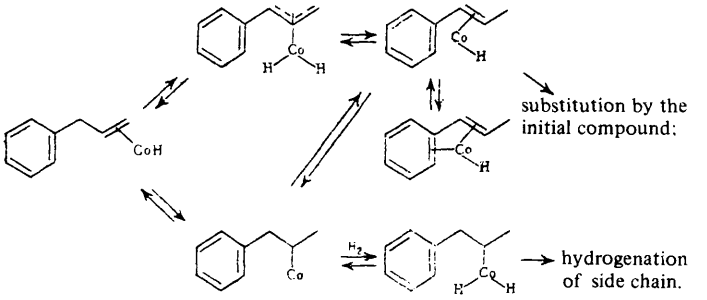
It has been shown that the 14-electron complex, capable of interacting with arenes as η^4-ligands, is catalytically active.

The hydrogenation and deuteriation of aromatic alkyl derivatives in the presence of η^3-$C_3H_5Co[P(OCH_3)_3]_3$ has also been studied.[52] The occurrence of *cis*-deuteriation and of the H–D exchange involving the n-alkyl substituents has been noted; the t-butyl substituent is not deuteriated. Alkyl- and alkenyl-cyclohexenes are formed in the presence of hexene.

The deuteriation of the side chain in substituted benzenes proceeds via the formation of the intermediate complex



according to Bleeke and Muetterties.[52] The same workers[52] explained the complex composition of the allylbenzene hydrogenation products by competing reactions involving the isomerisation of the intermediates and their displacement by the starting material in accordance with the following mechanism:



It has been shown[52] that η^3-$C_8H_{13}Co[P(OCH_3)_3]_3$ also catalyses the hydrogenation of benzene and a rapid stage involving the elimination of η^3-cyclo-octenyl ligand is observed. The hydrogenation mechanism proposed by Hirsecorn et al.[48] has been revised on the basis of the study of the intermediates in the hydrogenation of toluene in the presence of this complex.

According to Bleeke and Muetterties,[52] the catalytically active species is formed via the mechanism

$$\eta^3\text{-}C_8H_{13}Co[P(OCH_3)_3]_3 \rightleftarrows \underset{\text{(VI)}}{\eta^3\text{-}C_8H_{13}Co[P(OR)_3]_2} + P(OR)_3 ;$$

$$\text{(VI)} \xrightarrow{H_2} \underset{\text{(VII)}}{HCo[P(OR)_3]_2} + C_8H_8 ;$$

$$\text{(VII)} \xrightarrow{P(OR)_3} \underset{\text{(VIII)}}{HCo[P(OR)_3]_3} \overset{H_2}{\rightleftarrows} \underset{\text{(IX)}}{H_2Co[P(OR)_3]_3} ;$$

$$\text{(VIII)} \xrightarrow{P(OR)_3} \underset{\text{(X)}}{HCo[P(OR)_3]_4} .$$

In the absence of the arene, the inactive complexes (IX) and (X) are obtained, while in its presence hydrogenation takes place via the mechanism

$$HCo[P(OR)_3]_2\ (\eta^4\text{-}C_8H_8) \rightleftarrows \eta^3\text{-}C_8H_{13}Co[P(OR)_3]_2 \overset{H_2}{\rightleftarrows}$$
$$\rightleftarrows \eta^3\text{-}C_8H_{13}CoH_2[P(OR)_3]_2 \rightleftarrows HCo[P(OR)_3]_2\ (\eta^4\text{-}C_8H_8) \text{ etc.}$$

The main disadvantages of the η^3-$C_3H_5Co[P(OCH_3)_3]_3$ catalyst are its low stability and low activity.

Attempts have been made[53] to increase the stability and activity of the complexes by varying the ligand environment. The relative rates of hydrogenation of benzene in the presence of a series of phosphine and phosphite complexes are as follows:

η^3-$C_3H_5Co[P(OCH_3)_3]_3$ (1), η^3-$C_3H_5Co[P(OC_2H_5)_3]_3$ (2),
η^3-$C_3H_5Co[P(OCH_3)_3]_2P(OC_3H_7\text{-iso})_3$(4),
η^3-$C_3H_5Co[P(CH_3)_3]_3$ (5), η^3-$C_3H_5Co[P(OC_3H_7\text{-iso})_3]_3$ (30),
η^3-$C_3H_5Co(CO)_3$ (0), $ONCo[P(OC_3H_7)_3]_3$ (0).

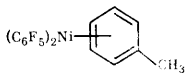
The increase of the activity of the complex was accompanied by a decrease of its stability. The complexes investigated contain the allyl ligand, which reacts readily ($\eta^x \rightleftarrows \eta^{x-2}$) as well as phosphine or phosphite ligands, which ensure a high electron density at the metal atom promoting the activation of H_2, and dissociate with a low activation energy.

However, the suggested intermediate $C_3H_5CoH_2L_3$ decomposes readily to an inactive hydride. Therefore a more stable catalyst would be one containing an η^x-ligand or a redox-ligand, which has either undergone ready conversion into the η^{x-2}-form or has been involved in electron transfer between the metal and the ligand; these transformations must not be accompanied by the elimination of the H ligand. The ON ligand, for example, is of this type but the complex containing it proved to be inactive in hydrogenation.[53]

It has been possible to synthesise the stable complex[54] η^6-$C_6(CH_3)_6$Ru-η^4-$C_6(CH_3)_6$, which is capable of catalysing the hydrogenation of benzene at 90 °C and a pressure of 2–3 atm. The hexamethylbenzene ligand proved to be resistant to both hydrogenation and competitive displacement by the substrate and the reaction products. The stereoselectivity of the complex was found to be lower than that of η^3-$C_3H_5Co[P(OCH_3)_3]_3$. The ratio of the *cis*- and *trans*-isomers is 9 : 1 and 9 : 2 respectively after the hydrogenation of *o*- and *p*-xylenes. In the hydrogenation of benzene and xylenes considerable amounts of cyclo-olefins were detected. For benzene, *o*-xylene, and *p*-xylene, the amounts are 5, 40, and 55% respectively. In the presence of η^6-$C_6(CH_3)_6$Ru-η^4-$C_6(CH_3)_6$, intense H–D exchange takes place. The hydrogenation of C_6D_6 and the deuteriation of C_6H_6 involve the formation of cyclohexanes containing between zero and 12 deuterium atoms, $C_6H_6D_6$ predominating. The catalyst ligands are also deuteriated. The deuteriation of the alkyl substituent predominates in toluene.[54]

The stability of the complex is determined by the resistance of the ligands to reduction by hydrogen. The transition of the arene to the η^4-state in bis(hexamethylbenzene)ruthenium(0) requires a low activation energy (16 kcal mole^{-1}).[55] In complexes where the activation energy for this process is higher, the hydrogenation of benzene is difficult, as happens for example, in the case of $CH_3C_6H_5TiAl_2Cl_8$.[55]

η^6-Toluenebis(pentafluorophenyl)nickel(II) proved to be a catalyst capable of hydrogenating benzene and toluene at 100 atm at 25 °C:[56]



It is fairly unstable and decomposes with formation of nickel and C_6F_5H.

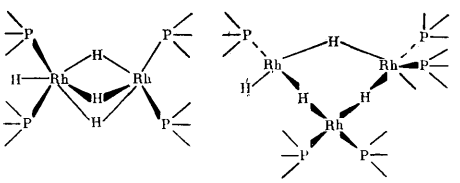
The reduction of the complex $RuCl_2(C_6Me_6)(PPh_3)$ with sodium tetrahydroborate, lithium tetrahydroaluminate, or an isopropyl alcohol solution of sodium carbonate leads to the formation of $RuHCl(C_6Me_6)(PPh_3)$, which is capable of hydrogenating benzene even at room temperature.

Treatment of the complex $[RuCl_2(\eta^6\text{-}C_6Me_6)]_2$ with a solution of sodium carbonate in isopropyl alcohol makes it possible to obtain the complex $[(\eta^6\text{-}C_6Me_6)Ru(\mu\text{-}H_2)(\mu\text{-}Cl)Ru(\eta^6\text{-}C_6Me_6)]Cl$. Benzene is hydrogenated to cyclohexane in the presence of this catalyst, the turnover number of the reaction amounting to 4.1 min^{-1}. At 50 °C and a pressure of 50 atm in the course of 36 h, the catalyst effects the quantitative hydrogenation of styrene to ethylcyclohexane, of anisole to methoxycyclohexane, of methyl benzoate to methyl cyclohexanoate, and of acetophenone and benzophenone to the corresponding cyclohexyl ketones. The hydrogenation of phenol to cyclohexanol, of nitrobenzene to aniline, of dimethylaniline to cyclohexylamine, and of phenylacetylene to ethylbenzene and styrene proceeded less vigorously.[58] Halogenobenzenes were converted into cyclohexane. The halogeno-substituent was retained in the cyclohexane ring only in the case of fluorobenzene.[58]

The complex η^3-$C_3H_5RhL_2$, where L = $P(OC_3H_7\text{-iso})_3$, is an extremely short-lived catalyst of the hydrogenation of aromatic hydrocarbons.[59] The complexes where L = $P(OEt)_3$ and $P(OMe)_3$ are inactive. The above complexes interact with hydrogen in accordance with the mechanism

$$6H_2 + 3\,\eta^3\text{-}C_3H_5RhL_2 \rightarrow 3C_3H_8 + (HRhL_2)_3;$$
$$7H_2 + 3\,\eta^3\text{-}C_3H_5RhL'_2 \rightarrow 3C_3H_8 + H_3RhL'_4 + (HRhL'_2)_2.$$

The clusters formed under these conditions are capable of catalysing the hydrogenation of benzene and alkylbenzenes to the corresponding cyclohexanes. The hydrogenation of *p*-xylene proceeds with the intermediate formation of *cis*-1,4-dimethylcyclohexane, while *o*-xylene is hydrogenated more slowly, the *cis*- and *trans*-isomers being formed in equimolar amounts. In the hydrogenation of benzene derivatives containing unsaturated substituents of the olefinic type, both the aromatic ring and the substituent are reduced. It is of interest to note that the above compounds prevent the hydrogenation of benzene when they are introduced jointly into the reaction mixture.[60] Deuteriation in the presence of these complexes involves vigorous deuterium–hydrogen exchange. According to Sivak and Muetterties,[60] the bridged hydrides



function as the catalytic species.

The *p*-tolyl complexes $(p\text{-tol})_4Cu_2Rh_2$ and $(p\text{-tol})_4Au_2Rh_2$ are active in the hydrogenation of benzene and naphthalene at 1 atm at 20 °C.[61]

$(RhCl.cyclo\text{-}octadiene)_2$, reduced with an equimolar amount of n-butyl-lithium, catalyses the hydrogenation of benzene to cyclohexane and of naphthalene to *cis*- and *trans*-decalins under normal conditions; styrene and phenylacetylene are reduced to ethylcyclohexane, while stilbene is reduced to 1,2-dicyclohexylethane.[62]

A complex of analogous activity has been obtained by the reaction[63]

$$RhCl(H_2C{=}CH_2)_2 + \text{n-BuAuLiEt}_2O \rightarrow Au^0/Rh^0.$$

Hydrogenation catalysts which incorporate unsaturated hydrocarbon ligands in the coordination sphere during the reaction or after appropriate treatment have been described in a number of investigations.[64–68]

The coupled hydrogenation of arenes together with alkenes or dienes has been achieved in the presence of the system $AlR_3 + Co(C_5H_7O_2)_2 + P(C_4H_9)_3$, where $C_5H_7O_2$ = acetylacetonate.[64] The hydrogenation of benzene is ten times faster than that of cyclohexene, which is formed in apreciable amounts together with cyclohexane in the benzene hydrogenation reaction. After the complete conversion of alkenes or dienes into saturated hydrocarbons, the hydrogenation of arenes ceases. The activity of the catalyst increases as the temperature is reduced from 30° to 5 °C. $H_3Co[P(C_4H_9)_3]_3$ also catalyses the joint hydrogenation of arenes and alkenes, but its activity is lower. σ-Alkylcobalt, containing one or two phosphite ligands and an arene, has been suggested as the catalytically active species.[64]

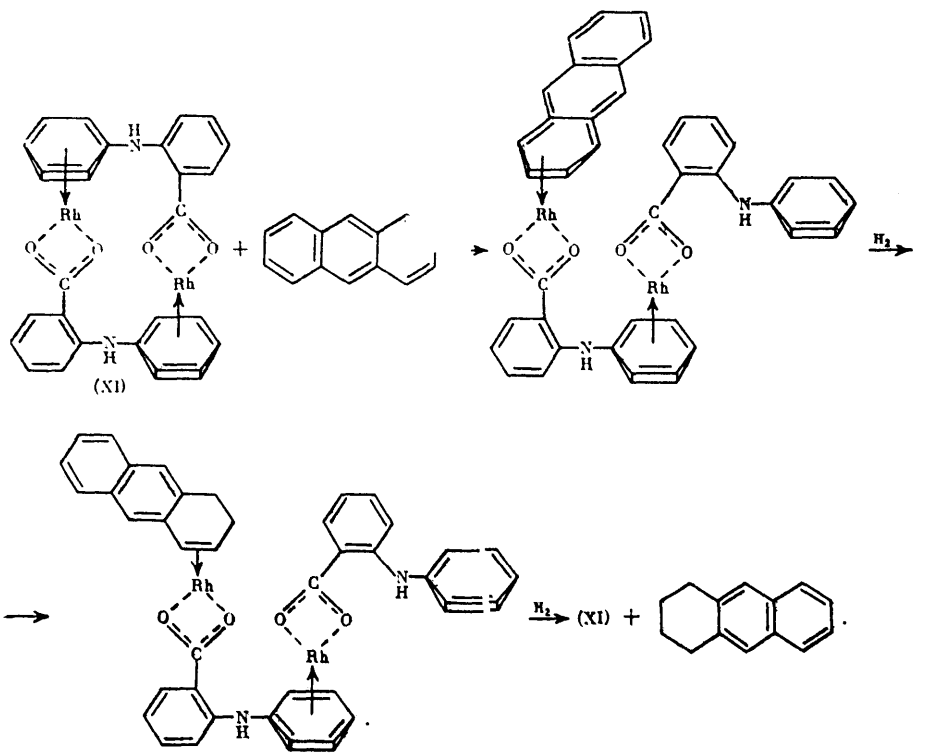
The complexes $(Al)(MR)Co(ML)_2$ (where Ar = aromatic hydrocarbons, R = alkyl, M = Li, MgBr, or AlR_2, and L = chelating ligands with carbonyl or imino-groups), $Co(PR_3)(RCH{=}CH_2)_2(AlEt_3)$ (where R = alkyl or aryl), and $Co(1,5,9\text{-}trans,trans,cis\text{-}C_{12}H_{18})(AlEt_3)$ are also capable of effecting the coupled hydrogenation of arenes and alkenes under mild conditions, benzene being hydrogenated to cyclohexene with a selectivity of 25–30%.[65]

Chlorotris(triphenylphosphine)rhodium (Wilkinson's complex) is incapable of catalysing the hydrogenation of aromatic compounds because of the presence of ligands with a tendency towards a dative interaction. However, the hydrogenation of benzene has been observed in the presence of Wilkinson's complex subjected to preliminary oxidation in a benzene solution. Cyclohexane is apparently formed as a result of the reduction of the aryl ligand in the intermediate oxidised complex.[66]

4. Metal Complexes with Ligands of the Aminoacid Type

The possibility of hydroxylating polycyclic aromatic compounds in the presence of rhodium complexes with strong π-donor systems such as naphthacene and *N*-phenylanthranilic acid has been demonstrated.[69] The rhodium complex of naphthacene makes it possible to hydrogenate the latter at 80 °C and a hydrogen pressure of 50 atm in dimethylformamide solution with formation of 1,2,3,4-tetrahydronaphthacene and a small amount of *sym*-octahydronaphthacene. Anthracene is hydrogenated to 1,2,3,4-tetrahydroanthracene under the same conditions in the presence of the rhodium complex of *N*-phenylanthranilic acid; the yields are fairly high also at room temperature and atmospheric pressure.[69]

The rhodium complexes of *N*-phenylanthranilic acid, other aminoacids, and aromatic carboxylic acids are active in the hydrogenation of naphthalene, phenol, and other aromatic hydrocarbons as well as their derivatives.[70–72] Experiments were performed at 20 °C and atmospheric pressure using a dimethylformamide solution of the catalyst. The initial rates of hydrogenation in the rhodium–*N*-phenylanthranilic acid system[72] decrease in the sequence anthracene > fluorene > fluoranthrene > naphthalene > pyrene > chrysene > benzene. Naphthalene is hydrogenated successfully to tetralin and decalin, benzene is hydrogenated to cyclohexane, and anthracene is hydrogenated to 1,2,3,4-tetrahydroanthracene. The structure of the complex was investigated by a wide variety of physicochemical methods.[73,74] A mechanism for the hydrogenation of anthracene has been proposed on the basis of investigations of the H–D exchange reaction of anthracene:[72]



In conclusion of the Sections devoted to the metal complex catalysts for the hydrogenation of aromatic hydrocarbons, it is necessary to consider catalytic systems of a kind which strictly speaking do not form part of any of the types examined.

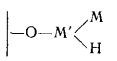
The chlorobishexa-1,5-dienerhodium complex has been used for the hydrogenation of arenes under conditions of catalysis with phase transfer.[75] The hydrogenation of a number of phenyl and benzyl ketones, benzene, phenol, and naphthalene has been investigated under mild conditions. The selectivity of the reaction was not always sufficiently high.

A system containing a hydrogen activator and a catalyst for the transfer of the activated hydrogen to the substrate has been proposed.[76,77] The use of Adams platinum as the hydrogen activator and titanium chloride complexes with various ethers as hydrogen transferring agents made it possible to hydrogenate benzene at room temperature and atmospheric pressure. Apart from cyclohexane, appreciable amounts of cyclohexene and cyclohexadiene are formed in the mixture and their relative amounts are not influenced by the duration of the hydrogenation process. Catalytically active species $[HTiL_{4-n}Cl^{+}_{n-1}]Pt$ arises in the reduction of the complex cation $TiL_{4-n}Cl^{+}_{n-1}$ by molecular hydrogen in the presence of PtO_2. The insertion of benzene in the Ti–H bond and the subsequent hydrogenation of the complex formed led to the formation of the reaction products.[76]

5. Polymer-containing Catalysts

The attempts to eliminate certain disadvantages of the homogeneous metal complex catalysts which limit their industrial application led to the creation of complexes containing organic and mineral polymers and macroligands. Whereas the mineral polymers are mainly used as heterogenising supports bound chemically to the metal complex, two applications are possible for organic polymers: either for the heterogenisation of the complex or for the synthesis of metal complexes with monodentate and polydentate macroligands whose solubility can often be varied reversibly depending on the stage of the process. A description of the properties of the metal-polymer complexes and the applications of catalysts can be found in other reviews.[78,79] The hydrogenation of aromatic hydrocarbons in the presence of these systems has been vigorously studied recently.

Systems which are tentatively similar to Ziegler catalysts and are capable of hydrogenating C_6–C_{30} aromatic hydrocarbons have been obtained by impregnating a suitable inorganic carrier having surface hydroxy-groups with a transition metal salt and subsequent treatment with trialkylaluminium or a similar compound.[80–82] A mechanism has been proposed[82] for the formation of intermediate active species of the type



where M = Fe, Ni, Co, or Cu and M′ is a Group I–III metal atom. Although the authors do not quote experimental data confirming rigorously the formation of such species, their hypothesis agrees with data obtained in a study[79] devoted to analogous catalysts.

In the interaction of polystyrene with (η^6-cyclo-octa-1,3,5-triene)(η^4-cyclo-octa-1,5-diene)ruthenium(0) the ligands are substituted by the benzene rings of polystyrene.[83,84] The resulting complex is an active catalyst of the hydrogenation of aromatic compounds (Table 5). Ru_2-1,3-diphenylpropane, obtained by a similar procedure from diphenylpropane, exhibits an analogous activity.[84] The increase of the number of benzene rings to more than two per metal atom lowers the activity of the catalyst.

Table 5. Hydrogenation of aromatic compounds in the presence of the Ru(0)–polystyrene catalyst.[83]

Substrate	a*	p_{H_2}, atm	t, °C	τ, h	Product**
Benzene	135	59	20	6	Cyclohexane
Benzene***	135	50	20	6	Cyclohexane
Toluene	90	50	20	6	Methylcyclohexane
Hexamethylbenzene	37	70	140	10	Hexamethylbenzene
Naphthalene	37	70	140	10	Naphthalene
Phenol	135	50	80	7	Cyclohexanol
Nitrobenzene	185	50	80	10	Cyclohexylamine

*Substrate : catalyst molar ratio.
**The content of the product or the substrate which failed to react is close to 100%.
***Re-use of the catalyst.

Table 6. Hydrogenation of aromatic compounds in the presence of the rhodium–anthranilic acid–polystyrene catalyst[90].

Substrate (content, mmol)	K*, mmol	τ, h	p_{H_2}, atm	t, °C	Product (yield, %)
Benzene (230)	3	18	3.4	20	Cyclohexane (99)
Benzene (230)	0.35	18	68	20	Cyclohexane (12)
Benzene (230)	0.35	5	68	100	Cyclohexane (25)
Benzene (230)	0.35	3	68	180	Cyclohexane (10)
Benzene (115)	0.044**	6	41	70	Cyclohexane (9)
Toluene (90)	0.2	18	3.4	20	Methylcyclohexane (15)
p-Xylene (160)	0.2	14	68	100	***
Ethyl benzoate (90)	0.2	20	68	100	****
Naphthalene (70) + benzene (110)	0.2	3	68	70	1,2,3,4-Tetrahydronaphthalene (100); cyclohexane (80)

*Amount of catalyst.
Catalyst stored in air for 1.5 years.
***Hydrogenation takes place to the extent of 10%.
Traces of hydrogenation.

A number of studies have been devoted to catalysts based on complexes of anthranilic and *N*-phenylanthranilic acid using polymeric macroligands. The rhodium and ruthenium complexes of *N*-phenylanthranilic acid, bound to phosphinated polystyrene or an inorganic carrier, catalyse the hydrogenation of benzene, anthracene, and 6-ethylchrysene.[85] The catalyst is obtained by the interaction of the finished complex with the carrier.

Another approach to the synthesis of the deposited complex is possible, namely by treating chloromethylated polystyrene with anthranilic or *N*-phenylanthranilic acid and then with a metal salt, this being followed by the reduction of the intermediate complex.[86–89] The catalyst prepared using *N*-phenylanthranilic acid did not show catalytic activity; an active catalyst was obtained from anthranilic acid. The rhodium and ruthenium catalysts effect the hydrogenation of benzene

at room temperature and a hydrogen pressure of approximately 2 atm. Under more severe conditions (100 °C, 20 atm H_2) the palladium catalyst permits the hydrogenation of benzene and *p*-xylene.

The rhodium complex of anthranilic acid bound to chlormethylated polystyrene has been studied in detail[90] (Table 6). According to the results of elemental analysis, the molar ratio of the anthranilate anions and rhodium in the catalyst is 3 : 1. The metal atoms are mainly distributed on the surface of the carrier. Only 3% of the chloromethylated groups of the initial polymer react with anthranilic acid. Analysis by X-ray electron spectroscopy (AXES) shows that the oxidation state of rhodium in the complex is +1. It is of interest that the nickel analogues are inactive in the hydrogenation of aromatic compounds.[91]

Table 7. Hydrogenation of aromatic compounds in the presence of rhodium complexes of carboxyl-containing polymers.[92,93,126]

Substrate	Polymer*	*t*, °C	*n***, h^{-1}	Reaction products (yield, %)
Benzene	STMC	30	51	Cyclohexane (100)
Benzene	PAA	30	85	Cyclohexane (100)
Toluene	PAA	20	19	Methylcyclohexane (100)
Nitrobenzene	STMC	30	11	Aniline (58)
Nitrobenzene	PAA	30	23	Aniline (77)
Phenol	STMC	50	34	Cyclohexanol (100)

*Here and henceforth PAA = polyacrylic acid and STMC = styrene–maleic acid copolymer.
**Turnover number of reaction.

Effective catalysts for the hydrogenation of the aromatic ring of benzene and its derivatives[92,93,126] (Table 7) have been obtained from rhodium complexes of carboxyl-containing polymers—such as polyacrylic acid and the styrene—maleic acid copolymer. The catalyst is prepared by adding rhodium tetrahydroborate to a solution containing the polymer and a rhodium salt. Under mild conditions (atmospheric pressure, 30 °C), it has been possible to hydrogenate benzene quantitatively to cyclohexane with a selectivity of 100%. The catalysts are extremely active in the hydrogenation of phenol to cyclohexanol and cyclohexanone. Apart from the reactions listed in Table 7, these catalysts are active in the hydrogenation of benzaldehyde, benzyl alcohol, and t-butylbenzene.

Treatment with hydrogen of the complex $Rh_2Cl_2(C_2H_4)_2$ deposited on chlormethylated and phosphinated cross-linked polystyrene[94] or of $Rh_2Cl_2(CO)_4$ deposited on the same polymer,[95] on SiO_2, or on polyphenylsiloxane, with both supports modified by phosphine groups,[96] leads to the formation of finely dispersed metallic rhodium which is active in the hydrogenation of benzene. Wilkinson's complex on modified SiO_2 and polyphenylsiloxane is not reduced and does not effect the hydrogenation of benzene.[96]

The formation of rhodium clusters has been detected in benzene solution following the interaction of $Rh_6(CO)_{16}$ with a film of cross-linked phosphinated polystyrene. At 80 °C and 1 atm the resulting catalyst reduces benzene with a low degree of conversion.[97] Aggregation of the clusters leads to an increase of the activity of the catalyst. The relation between the degree of aggregation of the hexa-atomic rhodium clusters and the catalytic activity has been studied.[98] The catalyst was prepared by impregnating silica gel with an $Rh_6(CO)_8$ solution and drying. Benzene was hydrogenated in a flow system. It has been shown[98] that particles with diameters less than 1.4 nm, consisting of six rhodium atoms, are catalytically inactive. The most active particles are 1.4–2.0 nm in size and contain 2–3 hexa-atomic clusters.

Catalysts having the general formula

$$\left[\left(\begin{array}{c}-CH_2-CH_2-N- \\ \\ R\end{array}\right)_n MX_q\right]_m$$

$R = H;\ C_{1-7}^{alkyl},\ C_6H_5CH_2CH_2,\ (CH_3)_3SiCH_2CH_2,$

$CH_3CO,\ C_6H_5CO;\ n = 2, 4, 8, 16,\ m = 4–200;$

$X = Cl, Br;\ q = 2, 4;\ M = Pt(IV), Pd(II), Ni(II), Co(II), Fe(III)$.

(the metal : nitrogen ratio varies from 1 : 2 to 1 : 16) are capable of effecting the quantitative hydrogenation of benzene to cyclohexane at 50 °C and a 100 atm pressure.[99]

The hydrogenation of *p*-nitrophenol at room temperature and atmospheric pressure with formation of 4-aminocyclohexanol has been described.[100] A catalyst prepared on the basis of rhodium, ruthenium, or iridium and polyvinylpyrrolidinone was used for this purpose.

Numerous studies have been devoted to the hydrogenation of aromatic compounds in the presence of metal complexes of polyamides. The first investigations in this field refer to the hydrogenation of benzene in the presence of a platinum–polyamide catalyst prepared on the basis of polymers obtained from caprolactam, hexamethylenediamine, and the β-lactam of β-aminosebacic acid.[101] A high yield of cyclohexene has been noted in some instances. The occurrence of two-point adsorption of benzene on the active centres has been suggested.

Dini et al.[102] also noted the selectivity of platinum–polyamide catalysts in the hydrogenation of benzene to cyclohexene. The reaction was carried out in a pulse apparatus at 140–190 °C. The authors explained the low degree of adsorption of hydrogen on the catalyst by the fact that the catalytically active species are compounds of platinum in which the degree of oxidation is non-zero.

The metal–nylon complexes catalysing the hydrogenation of benzene have been investigated.[103–106] Detailed study of the platinum–nylon complex[104] has shown that the optimum composition of the catalyst is attained when there are eight peptide groups per platinum atom. The authors suggest that it is unlikely that stable eight-membered chelate complexes are formed under the reaction conditions[104] and the complex apparently contains one peptide group. It has been shown that, when halogen substituents are introduced into the benzene ring, the rate of hydrogenation diminishes, which has been attributed to a decrease of the ionisation potential and the formation of an unduly stable substrate–catalyst complex.[102] Apart from the change in the ionisation potential of the substrate, steric hindrance plays a significant role in the hydrogenation of alkylbenzenes.

The hydrogenating activities of various metals in the nylon complexes have been examined.[105,106] It has been shown that the capacity for the formation of complexes with nylon varies in the sequence Pt > Pd > Rh > Ir, while the activities of the nylon complexes in the hydrogenation of benzene vary in the sequence Ir > Pt > Rh > Pd. The optimum ratio of the number of polyamide units to that of the metal atoms is four for rhodium and palladium, in contrast to platinum, the activity of the palladium complex proving very low in the hydrogenation of benzene. However, one should note that sufficiently rigorous evidence has not been presented[102–106] for the existence of complexes in the course of the reaction; one cannot rule out the possibility that the metallic phase is active.[107,108]

The hydrogenation of benzene on atomically dispersed platinum on nylon has been investigated[107,109] and the influence of the specific surface on the activity has been demonstrated.[107] The unusually high selectivity of the platinum–nylon catalyst with respect to cyclohexene has been explained by the weak adsorption of benzene on the catalyst.[109] It has been suggested that benzene forms a π-bond with only one metal atom. In this case hydrogen does not add as a result of a surface reaction (as in the metal) but involves the bonds conjugated with those participating in the formation of the π-complex. The double bond which has not been hydrogenated remains unavailable for the addition of hydrogen.

III. HYDROGENATION OF HETEROCYCLIC COMPOUNDS

Many fewer studies have been made of the hydrogenation of heterocyclic compounds on metal complex catalysts. The reason for this is apparently the risk that the formation of stable complexes of heterocycles with the metal ion might deactivate the complex. Since hydrogenation under severe hydroformylation conditions makes it possible to avoid the poisoning effect of even sulphur-containing heterocycles, this reaction has been studied to the greatest extent. Thus the hydrogenation of furan derivatives has been described.[21] At 180 °C and pressures of the H_2 + CO (2 : 1) mixture of about 200 atm in the presence of $Co_2(CO)_8$ furan is converted in the course of 4 h into 2-tetrahydrofurfuryl alcohol to the extent of 35%, while 2,5-dimethylfuran is converted into 2,5-dimethyltetrahydrofurfuryl alcohol to the extent of 23%.

The hydroformylation of 5,6-dihydro-4*H*-pyrans is accompanied by the saturation of the pyran ring.[110] The product consisted of 78% of 2-hydroxymethyltetrahydropyran, 8% of 3-hydroxymethyltetrahydropyran, and 3% of tetrahydropyran. In addition, reactions of other dihydropyrans have been investigated at a pressure of the mixture of equimolar amounts of carbon monoxide and hydrogen of 300 atm and a temperature of 190 °C in the presence of dicobalt octacarbonyl.[110]

Table 8. Hydrogenation of thiophen and its derivatives under hydroformylation conditions*.[111]

Substrate	a**	τ, h	Reaction product (yield, %)
Thiophen	14.7	5	Thiophan (50)
Thiophen	5.9	4	Thiophan (66)
2-Methylthiophen	22.7	5	2-Methylthiophan (77)
2-Ethylthiophen	9.1	3	2-Ethylthiophan (82)
2,5-Dimethylthiophen	18.3	5	2,5-Dimethylthiophan
2-Thenyl alcohol	15.0	4	2-Methylthiophen (24); 2-methylthiophan (57)
2-Acetylthiophen	15.6	9	2-Ethylthiophen (52); 2-ethylthiophan (26)

*Temperature 180 °C, pressure of H_2 : CO = 2 : 1 mixture 22 atm, catalyst–dicobalt octacarbonyl.
**Substrate : catalyst molar ratio calculated per metal atom.

The reduction of thiophen derivatives under hydroformylation conditions has been described[111] (Table 8). Sometimes cobalt is introduced in the form of the carbonate instead of the octacarbonyl, but in all cases the active species is cobalt hydrocarbonyl. It is especially interesting that substituted thiophens are reduced more readily than thiophen itself. It has been shown that the hydrogenation is irreversible, this being indicated by the stability of thiophan under the reaction conditions.[111]

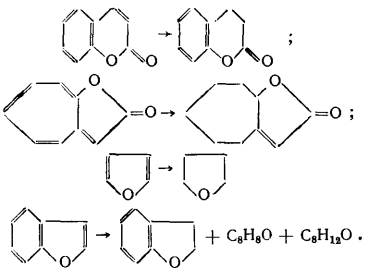
The hydrogenation of nitrogen-containing heterocycles has been investigated in the presence of various metal carbonyls and carbonyl phosphite complexes.[22,26,112–115] Pyridine is converted into a mixture of *N*-formyl- and methyl-pyridines at 200 °C under a pressure of an equimolar mixture of carbon monoxide and hydrogen of 410 atm.[112] At a lower pressure (213 atm), dihydro-derivatives of 2-methyl- and 2-phenylindoles have been obtained[113]. In both cases cobalt was introduced into the reaction mixture in the form of the metal or salts.

It has been shown[25,26,114,115] that the carbonyl and carbonyl phosphine complexes promote the preferential hydrogenation of the heteroring in bicyclic and polycyclic nitrogen-containing heterocycles.

Catalysts of the Ziegler type, which are also frequently used under severe conditions, have been used mainly for the hydrogenation of pyridine heterocycles. Thus the hydrogenation of pyridine to piperidine has been described.[32,34] Quinoline[116] is hydrogenated in the presence of cobalt acetylacetonate activated with AlR_3 (where R = alkyl or alkoxy-group) with formation of 78% of 1,2,3,4-tetrahydroquinoline, 9% of 5,6,7,8-tetrahydroquinoline, and 2% of decahydroquinoline (cobalt : aluminium = 10, H_2 pressure 68 atm, 90–100 °C). Only 17% of 1,2,3,4-tetrahydroquinoline is formed under the same conditions in the presence of diethyl sulphide.

The catalyst based on cobalt 2-ethylhexanoate makes it possible to hydrogenate furan to tetrahydrofuran to the extent of 95% at 20 °C and an H_2 pressure of 50–60 atm in the course of 4 h.[35]

Table 4 shows that the catalyst η^3-$C_3H_5Co[P(OCH_3)_3]_3$ is capable of hydrogenating oxygen-containing heterocycles under mild conditions.[49] The following reactions have been carried out using this catalyst:[49]

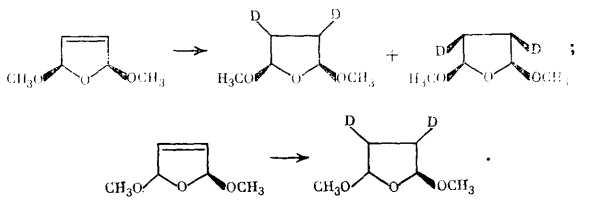


Overall, the hydrogenation is slow and the yields of reaction products are low.

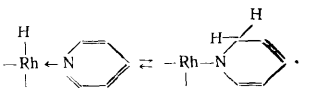
It has been stated[71,117] that the rhodium complexes of anthranilic and *N*-phenylanthranilic acids, L-tyrosine, aspartic acid, and α-piperidinoacetophenone oxime catalyse the hydrogenation of pyridine, quinoline, pyrrole, furan, dibenzofuran, and thiophen.

Chlorotris(triphenylphosphine)rhodium, which is known to be inactive in the hydrogenation of benzene, has been used for the stereoselective deuteriation of the double bond in

substituted 2,5-dihydrofurans.[118] 2,5-Dimethoxy-2,5-dihydrofurans are deuteriated in the *cis*-positions, the *cis*-isomer giving rise to a mixture of products:



Treatment of the complex $RhCl_3Py_3$ (where Py = pyridine) with sodium tetrahydroborate in dimethylformamide leads to the formation of $Py_2DMF.RhCl_2BH_4$.[119,120] The complex is capable of catalysing the reduction of pyridine to piperidine and of quinoline to 1,2,3,4-tetrahydroquinoline; the reaction proceeds under mild conditions at low rates. Isoquinoline and indole are not reduced. It is believed that the hydrogenation begins with hydrogen transfer:[20]



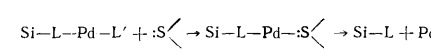
This is followed by the addition of hydrogen to the hydropyridine complex.

The hydrogenation of quinoline using metallophthalocyanine catalysts at temperatures in the range 300–400 °C and pressures up to 200 atm takes place selectively with formation of 1,2,3,4-tetrahydroquinoline.[121] The hydrogenation of thiophen and sulpholene in the presence of mononuclear and polynuclear palladium complexes containing ligands of different types linked to silica gel has been investigated.[122–124] Sulpholene is readily reduced to sulpholan, while thiophen is reduced with much more difficulty to thiophan (1 atm H_2, 20 °C, in isopropyl alcohol). The activation of H_2 has been suggested as the rate-limiting stage for the mononuclear complexes. Enhancement of the electron-donating properties of the ligand lowers the instability constant of the complex and the equilibrium concentration of the hydride formed in accordance with the equation

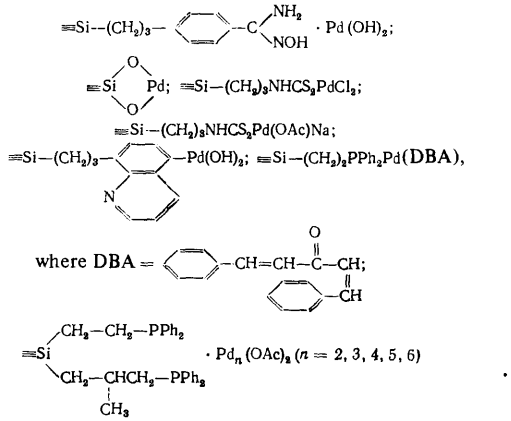
$$\equiv Si-L-Pd^{II} + H_2 \rightleftarrows [\equiv Si-L-Pd^{II}-H]^- + H^+.$$

The rate of hydrogenation of sulpholene is reduced as a consequence.

With increase of the number of palladium atoms in the cluster complex from 2 to 6, its activity in the hydrogenation of sulpholene also rises, but the activity in the hydrogenation of thiophen changes only slightly. The low activity of the catalysts in the hydrogenation of thiophen can be explained by the difficulty of activating the substrate and the poisoning of the catalyst by the reaction product, the complex being decomposed in certain instances in accordance with the mechanism



In the hydrogenation reaction in dimethylformamide, which is capable of entering into a complex formation reaction in competition with the metal, the catalysts are more stable. Enhancement of the electron-donating properties of the ligands in the mononuclear complexes promotes an increase of the stability of the complexes in the hydrogenation of thiophen, since the ability of the metal ion to coordinate to the sulphur heteroatom is then reduced.[122–124] The following compounds have been used as catalysts:



The catalysts prepared from carboxyl-containing polymers and platinum-group metal salts, which exhibited an activity in the hydrogenation of benzene, proved to be extremely active and selective in the hydrogenation of oxygen-containing compounds[92,93,125–128] (Table 9).

Table 9. Hydrogenation of heterocyclic compounds in the presence of catalysts prepared from carboxyl-containing polymers.[92,93,125–128]

Substrate	Catalyst*	t, °C	n**, h^{-1}	Reaction product (yield, %)
Furan	Rh-STMC	30	52	Tetrahydrofuran (100)
2-Methylfuran	Rh-STMC	30	113	2-Methyltetrahydrofuran (100)
Benzofuran	Pd-STMC	30	53	2,3-Dihydrobenzofuran (100)
1,4-Benzodioxan	Rh-PAA	30	7	Hexahydro-1,4-benzodioxan (32)
6-Nitro-1,3-benzodioxan	Rh-PAA	20	4	5-Amino-1,3-benzodioxan (75)
Furfural	Rh-PAA	20	44	Tetrahydrofurfuryl alcohol (96)

*For the significance of the abbreviations, see Table 7.
**The turnover number of the reaction.

Mention should also be made of the hydrogenation of pyridine, quinoline, and furan derivatives under the conditions of catalysis with phase transfer in the presence of rhodium complexes.[75] Fairly high yields of the hydrogenation products were then achieved.

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The above analysis of data for the hydrogenation of aromatic compounds in the presence of metal complex catalysts shows that, despite the large amount of experimental data available, the possibilities for the selection of effective catalysts for the hydrogenation of aromatic hydrocarbons are small. The point is that the rational employment of metal complex catalysts requires the use of comparatively mild conditions, whereupon their ability to propagate processes at high rates is most fully realised, the process being at the same time highly selective and involving a small expenditure of energy. However, the use of active catalysts for the hydrogenation of the above compounds, such as the hydroformylation Ziegler catalysts and some of the complexes

with unsaturated hydrocarbon ligands, requires fairly severe reaction conditions. On the other hand, complexes active under mild conditions are frequently relatively unstable.

In the case of heterocyclic compounds the choice of metal complex hydrogenation catalysts is still more limited apparently owing to the low stability of the majority of the metal complexes investigated and acted upon by heterocycles. The successful solution of this problem involves the selection of a suitable ligand environment for the metal ion, which would stabilise it in the catalytically active state and would thus counteract the poisoning effect of the heterocycle; such stabilising activity of certain ligands can be demonstrated in the deuterium–hydrogen exchange involving thiophen and its derivatives.[15]

Overall, among the catalysts considered in this review, the most stable and effective under mild conditions and sufficiently universal is the rhodium complex of *N*-phenylanthranilic acid. Effective and "technological" catalysts on a polymer carrier have been based on it and it has been established reliably that the metal in such catalysts is in fact present in the form of a complex.

Catalysts based on carboxyl-containing polymers have also exhibited a high activity in the hydrogenation of aromatic and heterocyclic compounds under mild conditions.

The instances quoted above of the successful application of polymer-containing complexes in the hydrogenation of aromatic and heteroaromatic compounds show that the most promising procedure is the creation of effective metal complex catalysts on the basis of polymer-containing complexes, particularly with organic polymers and copolymers, which not only make it possible to heterogenise the catalyst when this is necessary but also can ensure its high stability by functioning as polydentate macroligands.

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Intermediate Compounds and Intermediate Reactions in the Synthesis of Oligonucleotides

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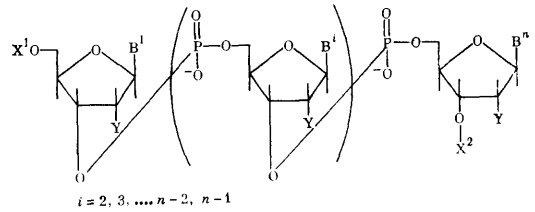
The principal features of the phosphorylation of nucleosides and other alcohols by phosphoric acid monoesters and diesters in the presence of the most widely used condensing agents (arenesulphonyl chlorides, arenesulphonyl azolides, carbodiimides, mixtures of arenesulphonyl chlorides with azoles and pyridines) are described. Data concerning the intermediate compounds and intermediate reactions in the oligonucleotides synthesis as well as model processes, obtained mainly with the aid of ^{31}P NMR, are discussed.
The bibliography includes 67 references.

CONTENTS

I. Introduction 185
II. The principal stages of phosphoester condensations 185
III. The interaction of the P-component with condensing agents 187
IV. Pyridinium derivatives and azolides of phosphoesters 190
V. The mechanism of the phosphodiester condensations 192
VI. The mechanism of the phosphotriester condensations 195

I. INTRODUCTION

Oligonucleotides having the general structure



$i = 2, 3, \ldots, n-2, n-1$

[X^1 and X^2 = H or $OP(O)O^-$, Y = H or OH, and B = nitrogen-containing heterocycles, usually adenine, guanine, cytosine, uracil and thymine] are fragments of the most important class of biopolymers—nucleic acids: DNA when K = H or RNA when Y = OH. Their chemical synthesis is one of the central tasks of bio-organic chemistry. Oligonucleotides are intermediate oligomers in the chemical-enzymic synthesis of genetic material. Their role as a research tool in molecular biology and genetic engineering has been continuously growing.

The main and frequently repeated stage in any method for oligonucleotide synthesis is the formation of new phosphoester (internucleotide) bonds between the monomers or the intermediate oligomers. Until recently, the main advances in the synthesis of oligonucleotides were achieved with the aid of phosphoester condensations, i.e. using the reaction between the hydroxy-group of one component (the OH-component) and the phosphate group of another component (the P-component), which takes place in the presence of condensing agents. Arenesulphonyl chlorides ($ArSO_2Cl$) and arenesulphonyl azolides [tetrazolides ($ArSO_2Tet$ and 3-nitro-1,2,4-triazolides ($ArSO_2NTr$)] have been most widely used as the latter. During the initial period of the establishment of the chemistry of oligonucleotides, dicyclohexylcarbodiimide (DCC) was widely used. Oxidation-reduction condensing agents, mainly a mixture of triphenylphosphine and di(2-pyridyl) disulphide have also been successfully employed.

The first serious advances in the chemical synthesis of oligonucleotides involved the development of the so-called phosphodiester method of synthesis in which the P-component is the phosphomonoester and the condensation product is the phosphodiester. Khorana and coworkers[1,2] achieved by this procedure the first syntheses of genes, using DCC and arenesulphonyl chlorides as the condensing agents. However, at the end of the 1970's there was an abrupt return to the phosphotriester method of synthesis in which the P-component is the diester and the condensation product is the triester. In the latter case the internucleotide phosphate is blocked by some kind of protective group, for example, the *p*-chlorophenyl group. Despite the necessity to remove the blocking groups from the internucleotide phosphate in the last stage, this has resulted in an overall significant simplification and acceleration of the synthetic procedure as a result of the acceleration of the intermediate condensations and the simplification of the purification of the intermediate oligomers. The employment of the phosphotriester method became effective as a result of the appearance of new condensing agents—arenesulphonyl azolides[3-8] and mixtures of arenesulphonyl chlorides with nucleophilic catalysts, namely tetrazole,[6] 3-nitro-1,2,4-triazole,[9,10] dimethylaminopyridine,[11-13] and *N*-methylimidazole.[10,14-19]

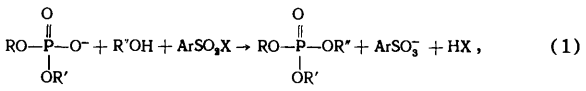
The importance of the phosphoester condensations in the chemistry of nucleotides led to interest in the study of their mechanism. A number of hypotheses concerning the nature of the intermediate species involved in these processes have been put forward by the founders of the chemistry of nucleic acids—Todd, Michelson, and Khorana. Systematic studies became possible following the appearance of the pulsed ^{31}P NMR method, which makes it possible to follow the course of the phosphoester condensations by recording the accumulation of the main and side products as well as certain intermediates.

The aim of the present review is to give an account of the present ideas about the mechanism of the formation of phosphoesters with the aid of condensing agents; these ideas are to a large extent based on studies of the intermediates and intermediate reactions in the oligonucleotide synthesis carried out by the authors of this review and their coworkers.

II. THE PRINCIPAL STAGES OF PHOSPHOESTER CONDENSATIONS

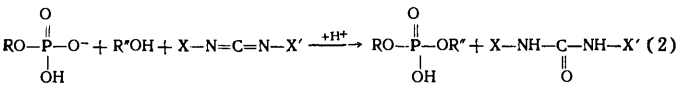
The phosphoester condensations are coupled reactions involving the formation of phosphoesters and transformations of the condensing agents. In the case of arenesulphonyl chlorides and arenesulphonyl azolides such a reaction is the

hydrolysis of the condensing agents and the overall condensation equation can be formulated thus:



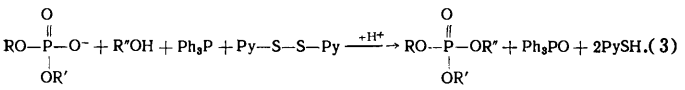
(1)

where X = Cl, the tetrazole residue, or the 3-nitro-1,2,4-triazole residue. In the case of DCC and other disubstituted carbodiimides, the formation of the phosphodiester is accompanied by the hydration of the condensing agent with formation of the corresponding disubstituted urea:



(2)

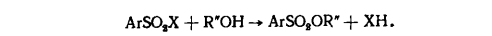
(for DCC, X, X' = cyclo-C_6H_{11}). In the oxidation-reduction condensation one component of the pair is reduced and the other is oxidised, for example:



(3)

In scheme (1) and (3) R' = H (for the phosphodiester condensation) or is an organic group (in the phosphotriester condensation). Depending on the solvents employed, the ions can exist as individual species or as ion pairs; here and below they are represented without the corresponding counterions.

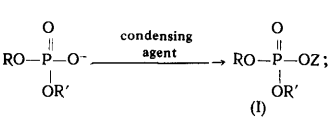
In conformity with the general ideas concerning the mechanisms of the coupled reactions,[20] reactions (1)–(3) should proceed via the formation of intermediates, which arise on interaction of the condensing agent (which behaves as the inductor) with one of the components to be condensed. It has come to be assumed that this interaction takes place with the P-component. The ability of all the condensing agents enumerated above to react with the P-component in the absence of the OH-component supports this view. On the other hand, these condensing agents either do not react at all with the OH-component under the conditions of phosphoester condensations, as happens in the case of DCC, or they are known *a priori* to give rise to side products. Thus arenesulphonyl chlorides and arenesulphonyl azolides sulphonate the OH-component via the reaction



However, hitherto it has not been possible to detect the products of the direct interaction of the condensing agents enumerated above with the P-component in any one instance; only the products of the subsequent reactions have been found.

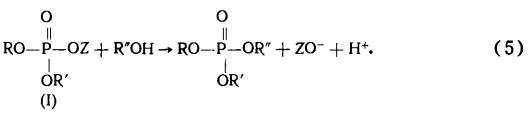
Thus the first problem which arises in the study of the mechanism of phosphoester condensations is that of the nature of the active intermediate species formed directly on interaction of the molecules of the condensing agent and the P-component and also of the mechanism of this interaction (see Section II).

It has been suggested[21] that the species formed are powerful electrophiles capable of phosphorylating the OH groups (Z is a fragment of the condensing agent):



(4)

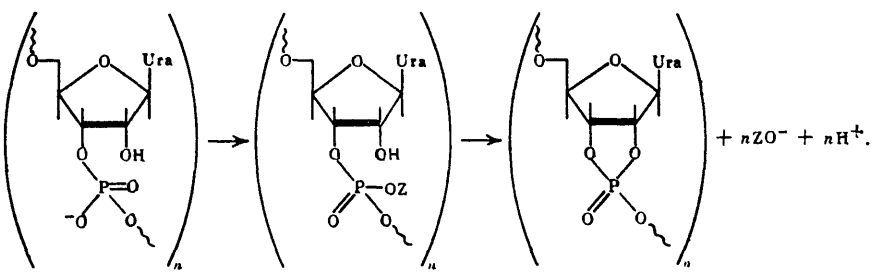
(I)



(5)

(I)

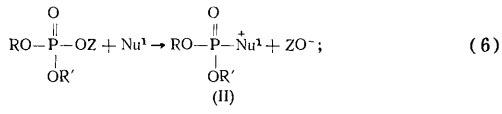
As an example of a process in the course of which the primary products of the interaction of the phosphate with the condensing agent are consumed mainly in the reaction with the OH groups, one may quote the interaction of the condensing agents triisopropylbenzenesulphonyl chloride (TPS) and DCC with the cetavlon salt of polyuridylic acid and dimethylformamide (DMF).[22] In both cases the disappearance of the signals due to the internucleotide phosphate and the appearance of signals of the cyclic phosphotriester groups, which have undergone a significant downfield shift, are observed in the ^{31}P NMR spectra, in conformity with the reaction in accordance with the scheme



The spatial proximity of the phosphate and 2'-hydroxy-groups favours reaction (5), which is in this instance intramolecular.

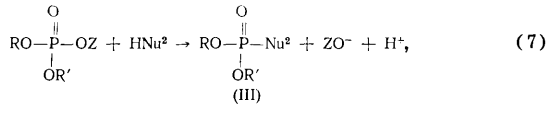
However, under the conditions of the formation of internucleotide bonds, this simple mechanism of the phosphoester condensation does not operate. In this case the reaction of the species (I) with the molecules of the OH-component is intermolecular and the system contains other nucleophiles more powerful than the OH-component.[2]

Among the nucleophiles competing with the OH-component for reaction with compound (I), mention should be made in the first place of pyridine, which has been used until very recently as the solvent,[21] in virtually all phosphoester condensations, and also certain other nitrogen-containing heterocycles, which have come to be employed in recent years to accelerate phosphoester condensations, namely tetrazole, 3-nitro-1,2,4-triazole, *N*-methylimidazole, and 4-*NN*-dimethylaminopyridine (DMAP). It is to be expected that in their presence the reaction proceeds preferentially via the following pathway:



(6)

(II)

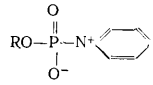


(7)

(III)

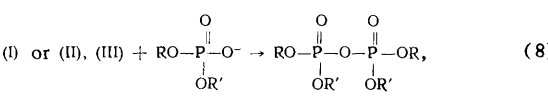
where Nu^1 = pyridine, 4,4-DMAP, or *N*-methylimidazole, HNu^2 = tetrazole or 3-nitro-1,2,4-triazole, R' = H or Ar, and R = protected nucleoside residue.

Compounds (II) and (III) should be fairly powerful phosphorylating agents, the former by virtue of the positive charge on the nitrogen atom and the latter as a result of the fairly high electron-accepting capacities of the tetrazole and nitrotriazole rings. The possible role of phosphorylpyridinium derivatives having the structure



as intermediates in phosphoester condensations has been pointed out by Michelson.[21] The second question of major importance for the understanding of the mechanisms of phosphoester condensations is therefore that of the role of compounds of types (II) and (III) and the formation of new phosphoester linkages, in first place of their reactivity in relation to alcohols. The data available on this question will be examined below (in Section III).

Together with the heterocyclic nucleophiles mentioned above, during the initial phase of the process the reaction mixture contains the P-component which has not reacted and which is also a nucleophile, as a rule stronger than the OH-component. The interaction of the molecules of the P- component with compounds (I)–(III) leads to their consumption with formation of pyrophosphate:

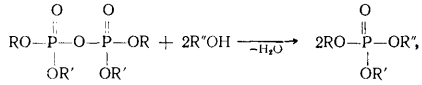


(8)

preventing thereby the formation of new phosphoester linkages. In the phosphotriester condensation this entails the formation of the pyrophosphotetraester, which lacks nucleophilic properties. Vigorous phosphorylation of the OH-component is possible only after the complete consumption of the P-component via reaction (8).

In the phosphodiester condensation the situation is significantly complicated as not only the initial P-component but also the pyrophosphodiester formed from it via reaction (8) and even the required reaction product (the phosphodiester) are nucleophiles. For the effective phosphorylation of the OH-component, it is necessary that both the P-component itself and all its nucleophilic derivatives should be fully exhausted. These reactions are described in Section (IV) in connection with the consideration of the general mechanism of the phosphodiester condensation.

As can be seen from the simplest example of reaction (8), in the first phase of the process the active intermediates of types (II) and (III) are consumed in the first place via their reactions with the P-component. In the second phase of the process, where new internucleotide bonds are mainly formed, the species (II) and (III) are regenerated from pyro- and poly-phosphates. This requires the involvement of nitrogen-containing heterocycles, which do not compete with the OH-component for compounds (II) and (III), since the interaction with these compounds is an exchange process which does not lead to the consumption of these species. Furthermore, the condensing agent can also participate in this process. For example, it follows from the stoichiometric equation of the reaction of pyrophosphodiester or pyrophosphotetraester with the OH-component,

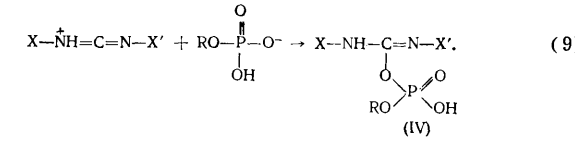


that the completion of the reaction requires the binding of the water molecule, i.e. the involvement of the condensing agent is essential.

The mechanisms of the regeneration of compounds (II) and (III) are also significantly different in phosphodiester and phosphotriester condensations; they will be considered separately in Sections (IV) and (V).

III. THE INTERACTION OF THE P-COMPONENT WITH CONDENSING AGENTS

According to Khorana,[23–25] in the case of disubstituted carbodiimides, the first condensing agents widely introduced into practical oligonucleotide chemistry, the primary product of the interaction of the P-component with the condensing agent is the corresponding *O*-phosphorylisourea (IV). Since phosphorylation in the presence of carbodiimides is strongly suppressed by basic amines, it has been suggested that the reaction proceeds between the protonated form of the carbodiimide and the phosphoester anion.[21,23–26]

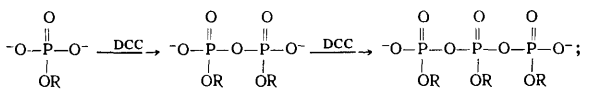


(9)

(IV)

However, compound (IV) could be neither isolated nor even detected in the reaction mixture. The primary product which can be isolated from the reaction mixture is the pyrophosphate. The subsequent reaction in the case of phosphomonoesters leads to the accumulation of trisubstituted triphosphate.[26] This result was subsequently used in other investigations[27–29] in which the reaction between 3'-acetylthymidine 5'-phosphate and DCC in pyridine was followed by

means of ^{31}P NMR, because the chemical shifts of the compounds formed, and in the case of the triphosphate also the structure of the spectrum, differ significantly and the behaviour of each component of the reaction mixture can be followed separately (Figs. 1 and 2):



R = 3'-acetyl-5'-thymidinyl.

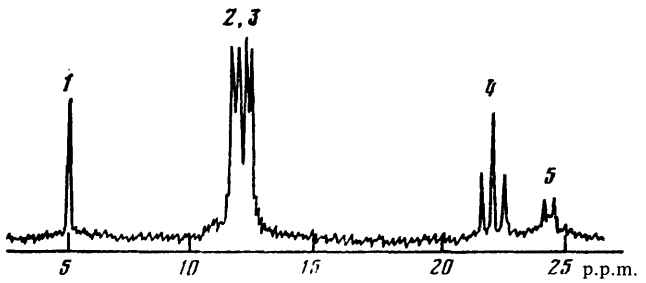


Figure 1. ^{31}P NMR spectrum of the reaction mixture obtained in the interaction of 0.15 M pT(Ac) with 1.5 M DCC in pyridine after 1 h from the start of the reaction: *1*) signal of the pyridinium derivative of pT(Ac); *2*) and *3*) signals of the terminal phosphorus atoms of the trinucleoside triphosphate and the tetranucleoside tetraphosphate; *4*) signals of the central phosphorus atom of the trinucleoside triphosphate; *5*) signals of the central phosphorus atoms of the tetranucleoside tetraphosphate.[37]

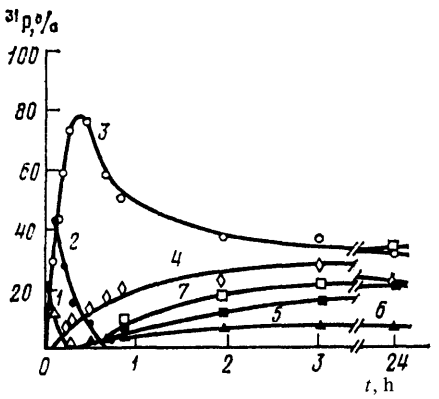
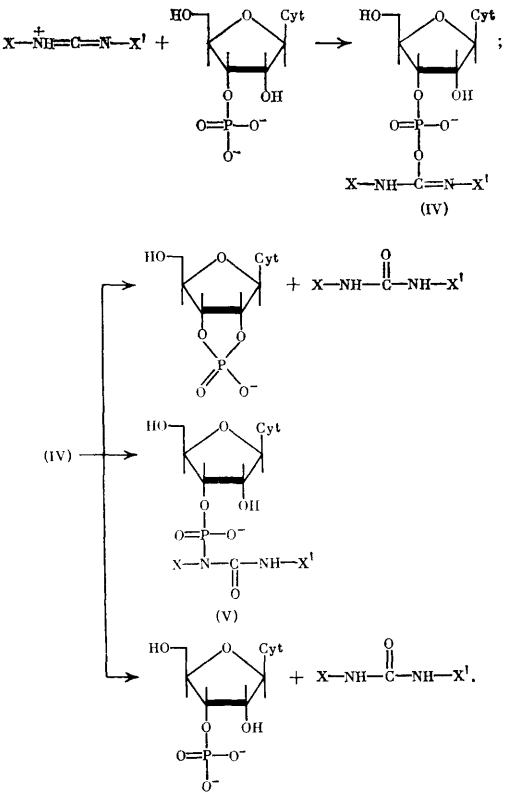


Figure 2. Kinetic curves for the interaction of 0.15 M Pt(Ac) with 1.5 M DCC in pyridine: *1*) initial mononucleotide; *2*) dinucleoside pyrophosphate; *3*) trinucleoside triphosphate; *4*) tetranucleoside tetraphosphate; *5*) *N*-pyrophosphorylurea; *6*) pyridinium derivative of pT(Ac); *7*) unidentified product.[37]

The kinetic test of mechanism (9) was carried out[30] in relation to the reaction of cytidine 2'(3')-monophosphate (CMP) with a water-soluble carbodiimide, namely *N*-cyclohexyl-*N'*-β-(*4-methylmorpholino*)*ethylcarbodiimide toluene-p-sulphonate* (henceforth abbreviated to CME-carbodiimide) in aqueous solution. In this case the reaction product is mainly cytidine cyclic 2',3'-phosphate (cCMP), which is apparently formed directly from the active intermediate (IV) as a result of the spatial proximity of the activated phosphate and the 2'-hydroxy-group. The formation of pyrophosphate is not observed in this instance. The accumulation of a certain amount of *N*-cytidylyl-ME-urea (V), which can be regarded as the product of the isomerisation of *O*-cytidylyl-CME-isourea (IV), was recorded.[30] It is significant that the rate of consumption of CME-carbodiimide is much higher than the rate of accumulation of the CMP reaction products. This shows that the reaction of CME-carbodiimide with CMP involves the formation of an intermediate, which, together with transformation into cCMP and compound (V), can hydrolyse with reformation of the initial CMP. In the light of the Khorana mechanism, the complete process mechanism can be represented as follows:

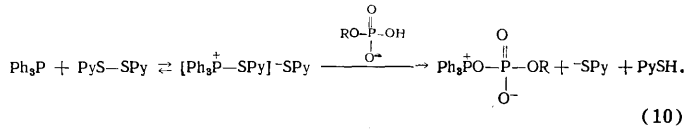


CME-carbodiimide is consumed via a first-order reaction with respect to both components, the effective reaction rate constant depending on the pH and the rate of reaction being proportional to the product of the concentrations of the protonated form of CME–carbodiimide and the double ionised form of CMP.[30]

In the reaction of CME–carbodiimide in aqueous solution with nucleoside 5'-phosphates at low concentrations of the latter, the hydration of carbodiimide is the main reaction pathway, in contrast to the reaction of nucleoside 2'(3')-CMP.[31] It has been shown[32] that, in the interaction of adenosine 5'-monophosphate, labelled with ^{18}O in the phosphate group, with DNA in pyridine in the presence of a large excess of $H_2^{16}O$, the labelled oxygen passes almost quantitatively to the dicyclohexylurea formed. This is also definite evidence in support of the intermediate formation of a compound of type (IV).

Thus all the available data agree with the mechanism proposed by Khorana and coworkers,[23–26] i.e. with the primary formation of *O*-phosphorylisourea.

The following mechanism of the formation of active phosphorylating species has been proposed for condensation in the presence of the triphenylphosphine–dipyridyl disulphide pair:[33,34]



(10)

The primary product detected by ^{31}P NMR in the case of 3′-*O*-acetylthymidine 5′-phosphate is, as in the case of carbodiimides, the corresponding pyrophosphate, which is subsequently converted into the triphosphate.[35] When dipyridyl disulphide is mixed with triphenylphosphine, no changes are observed in the ^{31}P NMR spectrum of the reaction mixture, which implies that, even if the process does proceed in accordance with scheme (10), the equilibrium in the first stage is strongly displaced to the left. The process has not been studied in detail.

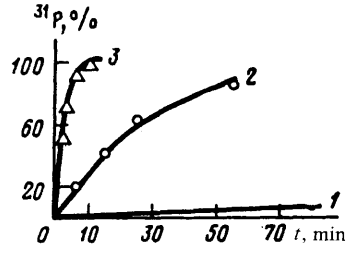
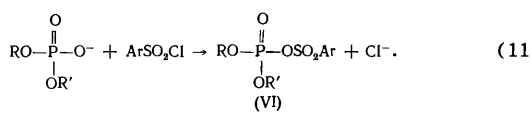


Figure 3. Kinetic curves for the formation of a tetrasubstituted pyrophosphate in the reaction of 0.1 M (ClC_6H_4). .pT(Lev)(triethylammonium salt) and 0.2 M TPS in chloroform at 30 °C in the presence of various additives: *1*) 0.4 M triethylamine; *2*) 0.4 M pyridine; *3*) 0.4 M *N*-methylimidazole.[18]

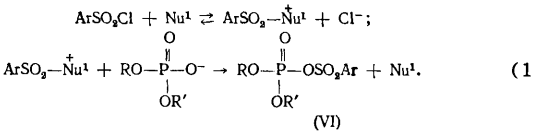
The first phase of the phosphoester condensation has been studied most thoroughly for arenesulphonyl chlorides and arenesulphonyl azolides. In both phosphodiester and phosphotriester condensations, the product of the interaction of the initial P-component with the condensing agent is the corresponding pyrophosphate.[17,27–29,36–43] In the reaction of phosphomonoesters with $ArSO_2Cl$, the pyrophosphodiester formed reacts to produce a trisubstituted triphosphate. The subsequent reactions of the latter will be considered in the next Section. The kinetics of the primary reaction with TPS have been investigated in the reaction involving 3′-O-acetylthymidine 5′-phosphate [pT(Ac)] and P^1P^2-di(3′-O-acetyl-5′-thymidinyl) pyrophosphate in pyridine. In both cases the reaction is of first order with respect to TPS and the P-component, which proves the involvement of only one molecule of the latter in the rate-limiting stage. This is in full agreement with the hypothesis of Corby, Todd, and Khorana,[44–46] according to which the primary product of the reaction of arenesulphonyl chloride with phosphates is a mixed anhydride of the phosphate and the arenesulphonic acid formed in accordance with the reaction



(11)

(VI)

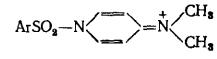
However, reaction (11) is complex and requires the participation of a nucleophilic catalyst.[18] It has been shown for the reaction of the p-chlorophenyl ester of 3′-*O*-levulinylthymidine 5′ phosphate [(ClC_6H_4)PT(Lev)] with TPS in a 7 : 1 chloroform–acetonitrile mixture that the formation of pyrophosphate is not detected at 30 °C in the course of 2 h, while in pyridine the process is completed in several minutes. Fig. 3 shows that the reaction is appreciably accelerated after the addition of a small excess (relative to TPS) of pyridine and to an even greater extent after the addition of *N*-methylimidazole; the addition of similar amounts of triethylamine leads merely to an insignificant accumulation of pyrophosphate. The nucleophilicity of these three bases varies in precisely the same sequence. Thus nucleophilic catalysis plays an appreciable role in the formation of the mixed anhydride (VI). The reaction apparently proceeds in accordance with the following mechanism:



(12)

(VI)

In conformity with this hypothesis, the application of the infrared spectroscopic method to a mixture of TPS or tosyl chloride with dimethylaminopyridine, which is also widely used as a nucleophilic catalyst, in methylene chloride revealed the formation of the arenesulphonyldimethylaminopyridinium derivative, which is apparently stabilised owing to the formation of a quinonoid structure:[47]



In the case of pyridine and *N*-methylimidazole such a derivative could not be detected, most probably because equilibrium (12) is greatly displaced to the left. Thus arenesulphonyl chlorides proved to be insufficiently powerful electrophiles to interact directly with the weakly nucleophilic anion of the phosphodiester, at least in solvents with a low dielectric constant.

The interaction apparently becomes possible with more nucleophilic phosphomonoesters in more polar solvents. Thus pT(Ac) reacts with TPS in DMF. However, the addition of pyridine significantly accelerates the reaction.[48]

The detected product of the interaction of arenesulphonyl azolides (the tetrazolide and 3-nitro-1,2,4-triazolide) with the P-component is also the corresponding pyrophosphate;[17,40–43] by analogy with the reaction of arenesulphonyl chlorides, one can suppose that the primary product is the same mixed anhydride (VI). In methylene chloride the interaction of (ClC_6H_4). .pT(Lev) with toluene-*p*-sulphonyl tetrazolide is slow but is significantly accelerated after the addition of pyridine.[43] Presumably in this instance the phosphodiester is sulphonated by the arenesulphonylpyridinium derivative. The formation of the pyrophosphate in pyridine on reaction of TsTet with (ClC_6H_4)pT(Ac) is significantly accelerated after the addition of toluenesulphonic acid and is almost fully blocked after the addition of an excess of triethylamine.[41] These effects agree well with the stoichiometric equation for the formation of the

arenesulphonylpyridinium derivative:

$$ArSO_2Tet + Nu^1 + PyH^+ \rightleftarrows ArSO_2\text{–}\overset{+}{N}u^1 + TetH + Py. \qquad (13)$$

Equilibrium (13) should be displaced to the left following the addition of a strongly basic amine and to the right after the addition of an acid.

The formation of the mixed anhydride (VI) is the rate-limiting stage in the formation of pyrophosphate. Kinetic measurements apparently do not make it possible to reach a definite conclusion concerning the mechanism of the subsequent transformation of compound (VI) into the pyrophosphate. It can take place either as a result of the direct interaction of compound (VI) with a second molecule of the P-component [Eqn.(14)][13,43] or via the preliminary formation of a phosphorylpyridinium or phosphorylazolium derivative [Eqns.(15) and (16)], as has been postulated in a number of investigations:[6,9,10,16]

$$RO\text{–}\overset{\overset{O}{\|}}{\underset{\underset{OR'}{|}}{P}}\text{–}O^- + RO\text{–}\overset{\overset{O}{\|}}{\underset{\underset{OR'}{|}}{P}}\text{–}O\text{–}SO_2Ar \rightarrow RO\text{–}\overset{\overset{O}{\|}}{\underset{\underset{OR'}{|}}{P}}\text{–}O\text{–}\overset{\overset{O}{\|}}{\underset{\underset{OR'}{|}}{P}}\text{–}OR + ArSO_3^-; \qquad (14)$$

(VI)

$$RO\text{–}\overset{\overset{O}{\|}}{\underset{\underset{OR'}{|}}{P}}\text{–}O\text{–}SO_2Ar + Nu^1 \rightleftarrows RO\text{–}\overset{\overset{O}{\|}}{\underset{\underset{OR'}{|}}{P}}\text{–}\overset{+}{N}u^1 + ArSO_3^-; \qquad (15)$$

$$RO\text{–}\overset{\overset{O}{\|}}{\underset{\underset{OR'}{|}}{P}}\text{–}\overset{+}{N}u^1 + RO\text{–}\overset{\overset{O}{\|}}{\underset{\underset{OR'}{|}}{P}}\text{–}O^- \rightleftarrows RO\text{–}\overset{\overset{O}{\|}}{\underset{\underset{OR'}{|}}{P}}\text{–}O\text{–}\overset{\overset{O}{\|}}{\underset{\underset{OR'}{|}}{P}}\text{–}OR + Nu^1. \qquad (16)$$

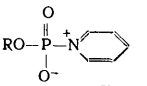
The sharp acceleration of the formation of the mixed anhydrides (VI) in the presence of pyridine and *N*-methylimidazole was interpreted above as a result of the significantly faster reaction (12) compared with the direct reaction (11). This means that the amines indicated are significantly more active than the phosphoester anions and attack the tetrahedral sulphur atom in $ArSO_2Cl$. It is logical to suppose that qualitatively the same relative rates obtain in the attack by the same nucleophiles on the tetrahedral phosphorus atom in compound (VI), i.e. reaction (15) predominates significantly over reaction (14) and the main pathway to the formation of the pyrophosphate is via stages (15) and (16).

In the case of phosphomonoesters the formation of the pyrophosphate and its subsequent conversion into the trisubstituted triphosphate and longer polyphosphates takes place on treatment with $ArSO_2Cl$ in DMF in the absence of nucleophilic catalysts. However, the addition of pyridine accelerates the process significantly, i.e. in the reaction with phosphomonoesters arenesulphonylpyridinium is also a stronger sulphonating agent than $ArSO_2Cl$.

IV. PYRIDINIUM DERIVATIVES AND AZOLIDES OF PHOSPHOESTERS

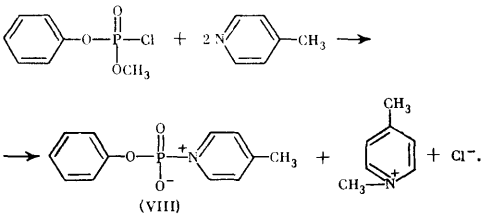
The most detailed information about the role of derivatives of type (II) as active intermediates phosphorylating the hydroxy-groups of the OH-component have been obtained in the study of the phosphodiester condensation in pyridine.

On treatment of phosphomonoesters (nucleoside 5'-phosphates, phenyl phosphate, nitrophenyl phosphate, etc.) with an excess of TPS[27–29] or with a cross-linked poly(styrenesulphonyl chloride) in pyridine,[49] ^{31}P NMR spectra revealed a virtually quantitative conversion of the esters into derivatives whose spectrum consisted of a singlet displaced upfield by ~5 p.p.m. compared with the initial ester. Detailed data for the chemical shifts and structure of the ^{31}P NMR spectra of phosphate esters and their derivatives have been published.[50] Nucleoside 5'-phosphates undergo the same reaction on treatment with an excess of a mixture of triphenylphosphine and dipyridyl disulphide in pyridine.[35,51,52] The comparatively slight change in the chemical shift on formation of these derivatives indicates the retention of the tetrahedral configuration of the phosphorus atom. The necessity for the presence of pyridine to ensure their formation suggests that they are phosphorylpyridinium derivatives having the structure



(VII)

Direct proof of this structure has been found for the derivative of phenyl phosphoric acid (VIII); which had been obtained by the following reaction for this purpose:[52,53]



(VIII)

The splitting of both the ^{31}P signal by the α-protons of the picolinium derivative and of the ^1H signal of the α-protons by the phosphorus nucleus ($^3J_{PNCH} = 5.5$ Hz) has been observed in the NMR spectra at −50 °C. This demonstrates the presence of a chemical bond between the phosphorus atoms and the γ-picoline residue. The chemical shifts for both the α-protons and the protons of the γ-methyl group are displaced downfield relative to picoline itself, which is due to the appearance of a positive charge near the picoline fragment. With increase of temperature, exchange is observed between free picoline and the derivative, which leads to the merging of the signals of both the α- and γ-methyl protons (Fig.4) in the spectra of free picoline and compound (VIII) and also to the disappearance of the splitting of the ^{31}P NMR signal by α-protons†.

At room temperature compound (VII) reacts vigorously with water, amines, phosphomonoesters, phosphodiesters, and substituted pyrophosphates, all the reactions reaching completion after less than 1–2 min (the time necessary to record the ^{31}P NMR spectrum.

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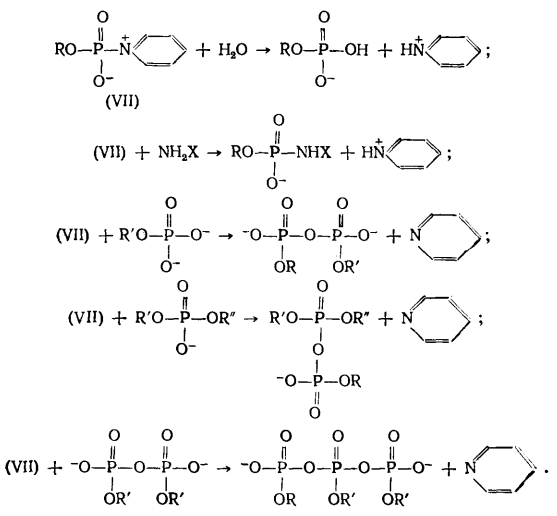
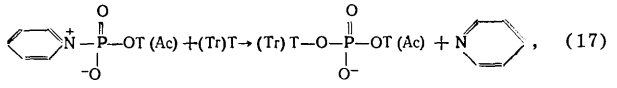
†The absence of such splitting under the conditions of the phosphoester condensations at room temperature in the presence of an excess of pyridine made it impossible in the first studies of the formation and reactions of compound (VII) to give preference to structure (VII) proposed by Michelson[21] and, in conformity with the hypothesis of Todd[45] and Khorana,[26,54] this compound was regarded as the corresponding metaphosphate $ROP\overset{O}{\underset{O}{\diagdown\!\!\diagup}}$.



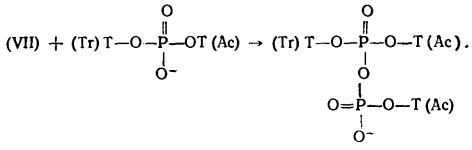
The reaction with alcohols takes place somewhat more slowly. In this instance it is possible to obtain with the aid of ^{31}P NMR the kinetic curve for the consumption of compound (VII) and to determine the rate constant. For the reaction



(17)

it amounts to 7.3×10^{-3} litre mol^{-1} at 30 °C and to 0.8×10^{-3} litre mol s^{-1} at 2 °C.[51] The rate constant depends significantly on the nature of the OH-component, which shows that the process proceeds via an associative mechanism. Thus the rate constant for the reaction of the same derivative at 2 °C with ethylenecyanohydrin is 11.3×10^{-3} litre mol^{-1} s^{-1}.[51]

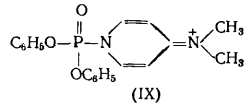
In the reaction of compound (VII) with alcohols the ^{31}P NMR spectra reveal the accumulation not of the phosphodiester but of the pyrophosphotriester—the product of the interaction of the phosphodiester formed with yet another molecule of compound (VII):



Pyrophosphotriesters have two non-equivalent phosphorus atoms, one of which is asymmetric; the ^{31}P NMR spectrum exhibits a complex signal, which consists of the superposition of the signals of two *AB* spin systems of two diastereoisomers[55,56] (Fig. 5).

It has been shown for the P-tetrazolide of pT(Ac) that the tetrazolides of phosphomonoesters are less reactive by at least two orders of magnitude on the analogous derivative of type (VII).[13]

The question of the reactivity of phosphodiester derivatives of types (II) and (III) has been investigated[11,12,40–43] on model systems—derivatives of diphenyl phosphoric acid obtained by treating diphenyl phosphorochloridate by the corresponding heterocycles. The 4-*NN*-dimethylaminopyridinium derivative was chosen as an example of a compound of type (II). When $(PhO)_2POCl$ is treated with DMAP in methylene chloride, the signal of the initial compound disappears from the ^{31}P NMR spectrum and another signal appears, which is split at −40 °C by the α-protons of the dimethylaminopyridinium fragment.[11] The signals of H_α, H_β, and CH_3 in the ^1H NMR spectrum are displaced downfield relative to the corresponding DMAP signals owing to the appearance of a positive charge in the DMAP fragment. This made it possible to identify the compounds formed as diphenyl phosphoryldimethylaminopyridinium derivatives, which apparently have the quinonoid structure



(IX)

Compound (IX) is extremely reactive with respect to alcohols. Thus the addition of ethylenecyanohydrin results in an almost instantaneous transformation into 2-cyanoethyl diphenyl phosphate.[11]

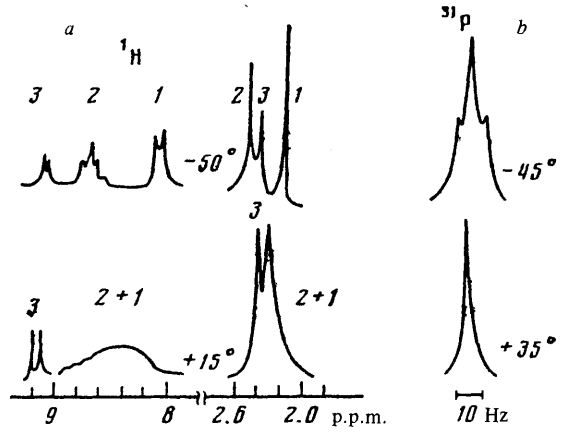


Figure 4. *a*) The structure of the ^1H NMR signals of the α-protons and γ-methyl groups as a function of temperature; *1*) of γ-picoline; *2*) of compound (VIII); *3*) of *N*-methyl-γ-picolinium; *b*) the structure of the ^{31}P NMR signals of compound (VIII) as a function of temperature. The spectra were recorded 1.5 h after the start of the reaction of phenyl methyl phosphorochloridate with 2 equivalents of γ-picoline in methylene chloride at room temperature.[52]

It must be emphasised that the analogous derivatives of phosphomonoesters are significantly less reactive with respect to alcohols than the pyridinium derivatives.[11–13] The greater stability of derivatives of DMAP is associated both with its higher basicity compared with pyridine and with the possibility of additional stabilisation via the formation of a quinonoid structure. The sharp increase of reactivity on passing from dimethylaminopyridinium derivatives of phosphomonoesters to derivatives of phosphodiesters is due to the fact that the former are zwitter-ions, while the latter carry an uncompensated positive charge.

Diphenyl phosphotetrazolide has been chosen as an example of compounds of type (III). When diphenyl phosphorochloridate is treated with tetrazole in dioxan in the presence of triethylamine, the ^{31}P NMR spectrum, measured after the precipitation of triethylammonium chloride, reveals a signal at 21.5 p.p.m., which differs significantly from that of the initial substance (5.5 p.p.m.).[41] The position of the signal makes it possible to identify the compound formed as diphenyl

phosphotetrazolide.[50] The addition of (Tr)T as the OH-component to the reaction mixture leads to the conversion of the tetrazolide of diphenylphosphoric acid into the corresponding phosphotriester (Tr)TOP(O)(OPh)$_2$. In the absence of bases the reaction is fairly slow. The data presented in Fig.(6) show that the reaction is significantly accelerated after the addition of pyridine and to an even greater extent after the addition of γ-collidine, which is a stronger base. The addition of triethylamine leads to an instantaneous conversion of the tetrazolide of the phosphodiester into the phosphotriester.[41,57]

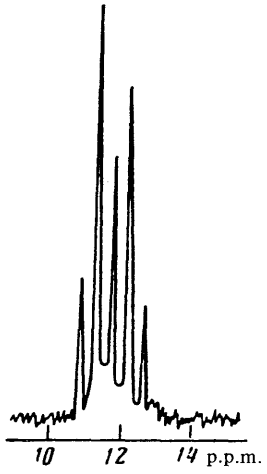


Figure 5. ^{31}P NMR spectrum of the pyrophosphotriester obtained on interaction of 0.0075 M (Tr)T with 0.15 M pyridinium derivative (VII) after 80 min from the start of the reaction.[29]

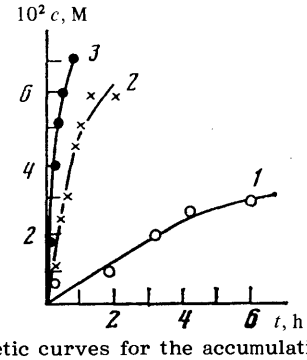


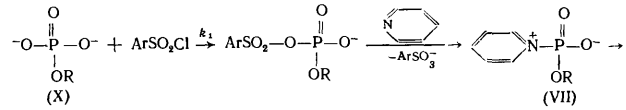
Figure 6. Kinetic curves for the accumulation of the phosphotriester (Tr)TOP(O)(OPh)$_2$ in the interaction of 0.08 M tetrazolide of diphenyl phosphoric acid with 0.01 M (Tr)T in dioxan at 30 °C: *1*) without additives; *2*) in the presence of 0.04 M pyridine; *3*) in the presence of 0.04 M γ-collidine.[57]

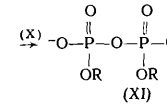
Thus species of types (II) and (III) are extremely reactive with respect to alcohols and there are grounds therefore for regarding them as the direct precursors of new phosphoester groups in phosphoester condensations.

V. THE MECHANISM OF PHOSPHODIESTER CONDENSATIONS

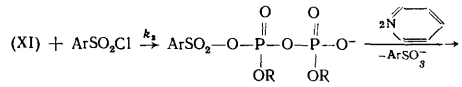
The mechanism of phosphodiester condensations has been investigated in greatest detail in relation to TPS as the condensing agent. The study of the complete system containing the P-component, the OH-component, and the condensing agent was preceded by a detailed investigation of the reaction of the P-component with the condensing agent in the absence of the OH-component. When 3′-*O*-acetylthymidine 5′-phosphate is acted upon by TPS in pyridine, the same sequence of reactions is initially recorded[27–29] as for DCC[58] (Fig.2).

It has been shown for the reaction of pT(Ac) and the pyrophosphate O[pT(Ac)]$_2$ formed from it that the order of the reaction with respect to both components is close to unity,[39,59] i.e. the rate-limiting stage of the process is the interaction of the condensing agent (apparently in the form of its pyridinium derivative) with one molecule of the phosphate or pyrophosphate. The product of the reaction of the pyrophosphate is triphosphate (XII). This indicates the conversion of the mixed anhydride of the pyrophosphate and the arenesulphonic acid into a mononucleotide derivative, which then attacks the pyrophosphate which has not yet reacted. After the consumption of the pyrophosphate, the accumulation of nucleoside 5′-phosphorylpyridinium in the reaction mixture begins. At the same time the accumulation of a certain amount of the tetrasubstituted tetraphosphate (XIII) is observed. Overall, the process kinetics can be described satisfactorily by the following scheme:

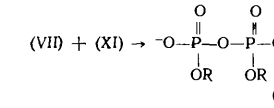


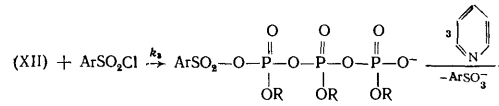


(18)

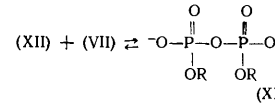


(19)





(20)



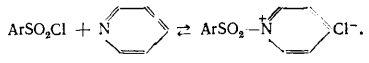
(21)

The Table presents the rate constants for the first three stages of the interaction of PT(Ac) and TPS at 5 °C and the entropies and enthalpies of activation estimated for these processes.[39]

In formulating reactions (18)–(21) and in calculating the rate constants for stages (18)–(20), no account was taken of the observed[46] significant accelerating effect of pyridine on the formation of pyrophosphates and polyphosphates. The species attacking the anions of the phosphomonoester (X), the pyrophosphate (XI), and the triphosphate (XII) is appar-

ently the arenesulphonylpyridinium cation $ArSO_2\overset{+}{N}\langle$. The rate constants listed in the Table are complex and represent the values of the true rate constants for the elementary

reactions of compounds (X)–(XII) with $ArSO_2-\overset{+}{N}$ multiplied by the constant concentration of pyridine and the equilibrium constant for the process

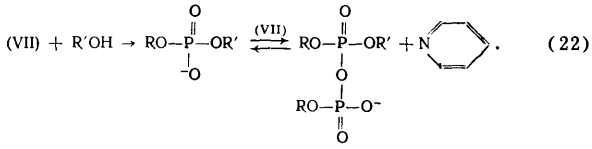


Kinetic parameters of reactions (18)–(20) at 5 °C.[39]

Reaction	$10^3 k$ litre mol^{-1} s^{-1}	$\Delta H^{\neq}$, kcal mol^{-1}	$\Delta S^{\neq}_0$, e.u.
(18)	11	9.8	−31.7
(19)	7	9.9	−32.6
(20)	1.1	9.7	−37.2

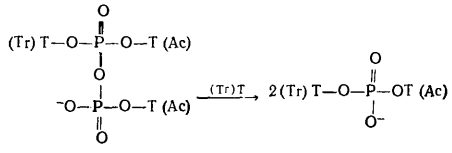
The pyrophosphate (XI) is only slightly less reactive with respect to TPS than the initial phosphomonoester.[59] The triphosphate is less reactive by an order of magnitude[59] and the decrease of the rate constant is largely associated with the decrease of the entropy of activation.

In the complete system the same sequence of transformations of the P-component is initially recorded. As compound (VII) appears in the reaction mixture, the formation of new internucleotide bonds becomes possible. However, as already stated, the phosphodiester formed reacts almost instantaneously with yet another molecule of compound (VII), forming the pyrophosphotriester (XIV):[55,56]

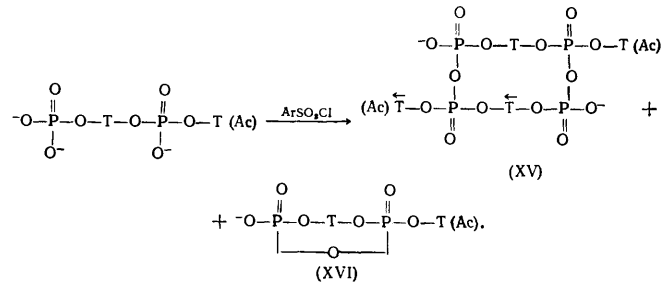


(22)

Pyrophosphotriesters are weak phosphorylating agents, the rate constants for the interaction of which with alcohols in pyridine are lower by two orders of magnitude than for the reactions of compound (VII) with the same alcohols. Thus the rate constant for the reaction



in pyridine at 30 °C is 9×10^{-5} litre mol^{-1} s^{-1}, while that for reaction (17) under the same conditions is 7.3×10^{-3} litre mol^{-1} s^{-1}.[39] Hence, even in the simplest case of the phosphodiester condensation designed to obtain a dinucleoside monophosphate, one of the two molecules of the two active phosphorylating derivative (VII) formed is converted into a significantly less reactive form. The situation is impaired even more when the P-component or the OH-component (or both) contains phosphodiester groups. If the OH-component is not a nucleoside but an oligonucleotide, compound (VII) formed from the P-component reacts in the first place with the phosphodiester groups and only when these have been converted into pyrophosphotriester groups does the reaction with hydroxy-groups proceed to an appreciable extent. Thus a large excess of compound (VII), which increases with increase of the length of the OH-component, is necessary.[38] On the other hand, when the P-component is an oligonucleotide, then, in the presence of a small excess of the condensing agent, pyrophosphotriester groups will form in it instead of the phosphorylpyridinium groups. When the dinucleotide pTpT(Ac) is acted upon by a small excess of TPS, the formation of compounds (XV) and (XVI) is mainly observed.[56–62] These are less reactive [the rate constants for the reactions with (Tr)T at 30 °C in pyridine are 0.6×10^{-4} and 2.8×10^{-4} litre mol^{-1} s^{-1} respectively]:[39]



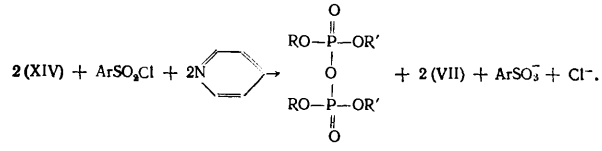
(XV)

(XVI)

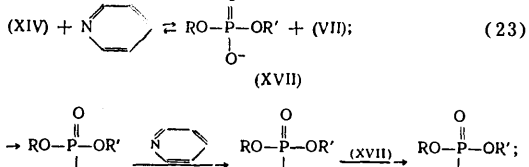
(The arrow above T denotes the direction from the 5′-OH group to the 3′-OH group of thymidine).

Compounds (XV) and (XVI), which have been obtained in DMF in the absence of pyridine, are so resistant to the action of nucleophiles that they can be separated chromatographically in aqueous solution.[62] There are therefore grounds for the assumption that their reaction with the OH-component in pyridine solution is feasible as a result of the nucleophilic catalysis by pyridine,[63] i.e. as a result of some reversibility of the second stage of reaction (22). This is also true of compound (XIV); as can be seen from the rate constants for the reactions of these pyrophosphotriesters with (Tr)T, for this purpose it is sufficient if less than 2% of compound (VII) is present in equilibrium with compounds (XIV), which is outside the limits of the sensitivity of the ^{31}P NMR method.

The highly reactive phosphorylpyridinium form is also regenerated from the pyrophosphotriester on treatment with an excess of the condensing agent.[55] The overall reaction is

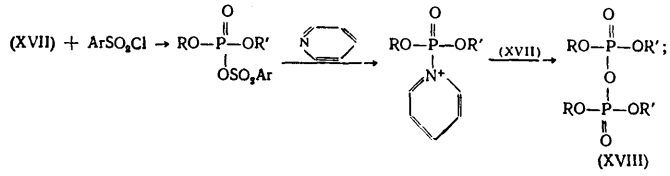


Its mechanism can be represented in the following manner:



(23)

(XVII)

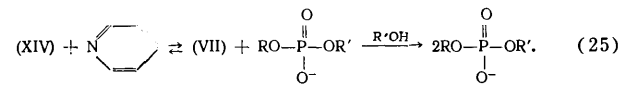


(XVIII)

R=(Tr)T, R′=T(Ac). (24)

It is noteworthy that the rate constant for the reaction of compound (XVII) with TPS, i.e. the rate-limiting stage of reaction (24), is 3.1×10^{-3} litre mol^{-1} s^{-1} at 5 °C, i.e. is only four times smaller than for the reaction with pT(Ac).[39]

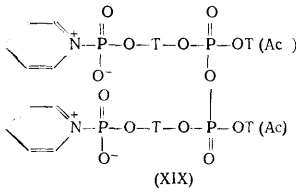
In the presence of a small excess of the condensing agent, when the rate of reaction (24) is low, the dominant pathway leading to the conversion of compound (XIV) into the diester may be the reaction



(25)

Reactions (23) and (24) lead to the conversion of the phosphodiester into the pyrophosphotetraester (XVIII), which can react to some extent with the OH-component, giving rise to the phosphotriester as the side product in the phosphodiester condensation.

The pyrophosphotriesters (XV) and (XVI) apparently undergo analogous reactions. In the presence of a sufficient excess of TPS, the dinucleotide pTpT(Ac) is converted into the compound[60-62]



(XIX)

containing the highly reactive phosphorylpyridinium groups [the rate constant for the reaction with (Tr)T at 30 °C is 6.3×10^{-3} litre mol^{-1} s^{-1}].[39]

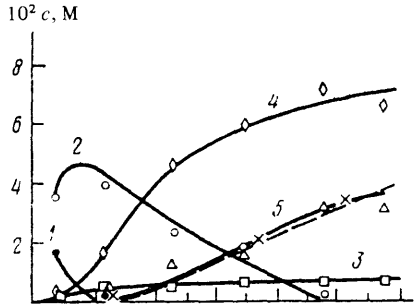
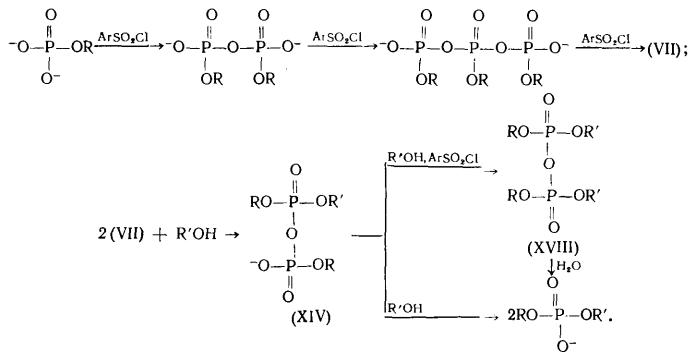


Figure 7. Kinetic curves for the interaction of 0.15 M Pt(Ac) with 0.15 M (Tr)T and 0.42 M TPS in pyridine: *1*) O[pT.(Ac)]$_2$; *2*) trinucleoside triphosphate; *3*) tetranucleoside tetraphosphate; *4*) pyridinium derivative of pT(Ac); *5*) the pyrophosphotriester (XIV).[51]

The reaction of compound (VII) with hydroxy-groups makes the main contribution to the formation of new phosphodiester groups.[52] Fig. 7 presents the kinetic curves for the accumulation of compounds (VII) and (XIV) in the reaction of pT(Ac) with (Tr)T in the presence of TPS at 2 °C. At the same time, the kinetic curve for the accumulation of compound (XIV) as a result of reaction (17), the rate-limiting stage in the formation of compound (XIV), has been calculated from the rate constant presented above for this reaction (dashed curve in Fig. 7). Evidently the calculated and experimental curves agree satisfactorily. Consequently the contribution of the reaction of the OH-component with other reactive species to the formation of phosphodiester is insignificant.

Thus even in the simplest case of the interaction of the P-component containing one phosphate fragment and the OH-component without phosphate groups, the mechanism of the phosphodiester condensations is fairly complex and is described by reactions (18)–(25), the majority of which consist of several elementary stages. The principal stages in the phosphodiester condensation in pyridine, detected by ^{31}P NMR, are presented schematically below:

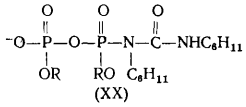


Regardless of the presence of the OH-component, the phosphomonoester undergoes a successive transformation into a substituted pyrophosphate and then into the corresponding triphosphate and the pyridinium derivative (VII). In the presence of the OH-component the derivative (VII) interacts with the latter via reaction (22), forming the trisubstituted pyrophosphate (XIV); the latter is capable of interacting with the OH-component, whereupon the phosphodiester accumulates but at a rate approximately eighty times lower than compound (VII).[39]

In the presence of a sufficient excess of the condensing agent reactions (23) and (24) result in the accumulation of compound (XVIII). However, when the reaction mixture is decomposed with water, this compound readily hydrolyses to the free phosphodiester.[36,58]

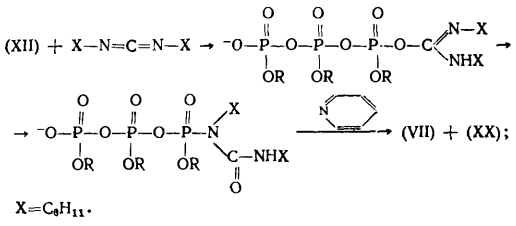
When pT(Ac) reacts in pyridine with a triphenylphosphine–dipyridyl sulphide mixture, the same sequence of transformations of the P-component to pyrophosphate, triphosphate, and finally the derivative (XIV) is observed.[51] The main pathway leading to the formation of phosphodiester group is in this instance also reaction (22).[51]

The reaction of pT(Ac) with DCC in pyridine is more complex. Both in the complete system and in the absence of the OH-component, the same sequence of transformations of the phosphomonoester into the corresponding pyrophosphate and triphosphate is observed. However, even in the absence of the OH-component, the final composition of the reaction mixture is more complex than for TPS and a triphenylphosphine–dipyridyl disulphide mixture. Together with compound (VII), a considerable amount of the triphosphate (XII) and the tetraphosphate (XIII) is retained and certain other derivatives, a considerable fraction of which consists of the ureido-derivative of the pyrophosphates (XX), are also detected:[58]



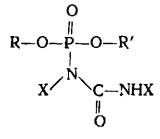
(XX)

This derivative, which should be regarded as the product of the isomerisation of the corresponding *O*-phosphoryldicyclohexylisourea in the light of Khorana's mechanism,[25] begins to accumulate after the complete consumption of the pyrophosphate, i.e. its formation is most probably associated with the reactions of the triphosphate. One of the possible mechanisms of such a reaction consists of this following sequence of stages:



$X = C_6H_{11}$.

When the reaction is carried out in the presence of the OH-component, the formation of compound (VII) is in fact not detected (Fig. 8) and the formation of compound (XX) is appreciably suppressed. By virtue of the absence of compound (VII), the free phosphodiester begins to accumulate in the system and is converted into the pyrophosphotetraester only to an insignificant extent. In the final reaction mixture most of the phosphodiester is present in the form of the ureido-derivative:



This derivative is only slowly hydrolysed by water to the corresponding phosphodiester and dicyclohexylurea.

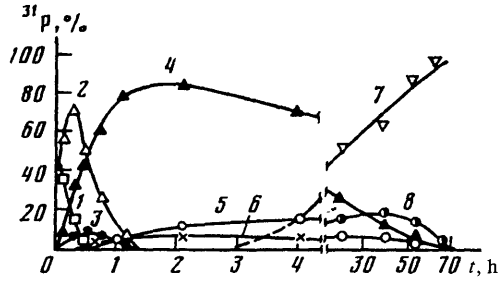
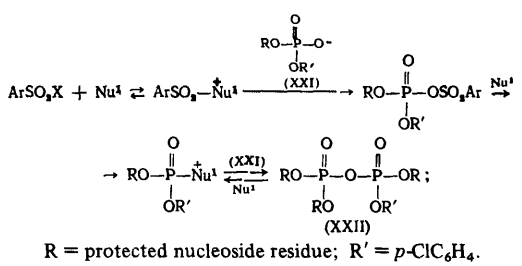


Figure 8. Kinetic curves for the interaction of 0.15 M pT(Ac) with 0.3 M (Tr)T and 1.5 M DCC at 22 °C in pyridine: *1*) the pyrophosphate O[pT(Ac)]$_2$; *2*) trinucleoside triphosphate; *3*) tetranucleoside tetraphosphate; *4*) the pyrophosphotriester (XIV); *5*) (Tr)TpT(Ac); *6*) signal intensity in the region of 5 p.p.m.; *7*) ureido-derivative of dinucleoside phosphate; *8*) the tetrasubstituted pyrophosphate (XVIII).[37]

VI. THE MECHANISM OF THE PHOSPHOTRIESTER CONDENSATIONS

Depending on the nature of the condensing agent, the first phase in the phosphotriester condensation is described by Eqn. (11) or (12) and then by Eqns. (15) and (16), i.e., overall, it can be represented by the equation



R = protected nucleoside residue; R′ = *p*-ClC$_6$H$_4$. (26)

This process is analogous to reaction (18) in the phosphodiester condensation. However, in contrast to this reaction, the pyrophosphate (XXII) does not undergo further transformations under the influence of the condensing agent, i.e. processes analogous to reactions (19)–(21) are absent in the phosphotriester condensation.

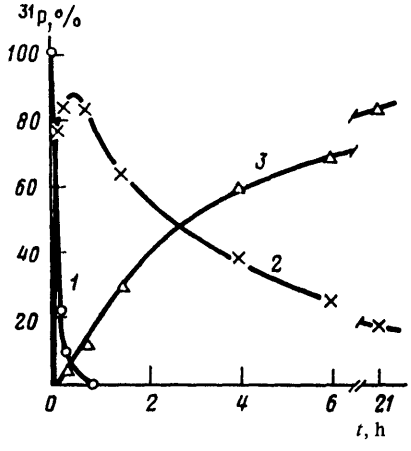


Figure 9. Kinetic curves for the reaction of 0.1 M (Tr)Tp.(C$_6$H$_4$Cl) with 0.1 M T(Ac) and 0.3 M TPS in pyridine at 30 °C: *1*) initial diester; *2*) the tetrasubstituted pyrophosphate (XXII); *3*) the triester (Tr)OTO – P(O)(OC$_6$H$_4$Cl) – OT(Ac).[42]

The inability of the pyrophosphate (XXII) to react with the condensing agent, except for the reaction analogous to reaction (19), necessitates at the same time the presence of another pathway leading to the transformation of the pyrophosphate into an active derivative of type (II) or (III). It is reasonable to suppose that this takes place analogously to the interaction of the pyrophosphotriester with the OH-component via a reaction analogous to reaction (25):

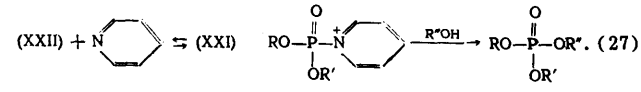


Fig. 9 presents the kinetic curves for the accumulation of the pyrophosphotetraester and the phosphotriester and for the consumption of the initial phosphodiester in the reaction of

(Tr)Tp(C_6H_4Cl) with T(Ac) in pyridine in the presence of a three-fold excess of TPS. The curves were obtained with the aid of ^{31}P NMR.[42] It is seen that, whereas the first phase of the reaction, i.e. the accumulation of the pyrophosphate, is completed in less than 1 h, the second phase takes more than 24 h. Such a prolonged contact of the OH-component with the condensing agent leads to undesirable side processes, for example, the sulphonation of the OH-component. There is no reason to doubt the extremely high electrophilicity of the species (XXIII), which carries an uncompensated positive charge. The low rate of the second phase of the reaction in pyridine is apparently associated with the fact that the species (XXIII), formed as an ion pair with the phosphodiester anion, interacts preferentially with the latter, which greatly displaces the equilibrium in the first reaction of process (27) to the left.

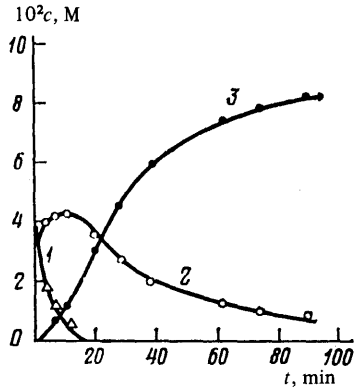
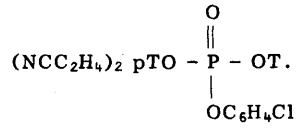


Figure 10. Kinetic curves for the interaction of 0.1 M (ClC_6H_4)pT(Ac) with 0.1 M (NCC_2H_4)$_2$pT, 0.3 M TPS, and 0.3 M tetrazole at 20 °C in pyridine: *1*) (ClC_6H_4)pT(Lev); *2*) the pyrophosphotetraester; *3*) the phosphotriester



[17]

In conformity with the foregoing, the effective catalysts of the second phase of the phosphotriester condensation proved to be compounds of two types. Firstly, these are compounds of the "pyridine" type, namely DMAP[12,13,17] and *N*-methylimidazole.[17,18] Being significantly stronger nucleophiles than pyridine, these compounds apparently give rise to species of type (II), which are significantly more stable than compounds (XXIII). Secondly, tetrazole[17,41,43] and 3-nitro-1,2,4-triazole[17] proved to be catalysts of this kind. They give rise to uncharged phosphodiester derivatives of type (III). As an illustration, Fig.10 presents kinetic curves for the reaction of (ClC_6H_4)pT(Lev) with (NCC_2H_4)$_2$pT in pyridine in the presence of a threefold excess of an equimolar mixture of TPS and tetrazole.[17] The reaction takes place to an extent greater than 70% in 1 h. As in the eactions of TPS in pyridine the absence of other catalytic additives, more than 90% of the pyrophosphate accumulates in the first phase of the reaction and the latter is then converted into the phosphotriester. In the light of these data, a sharp acceleration of the phosphotriester condensation following the replacement of arenesulphonyl chlorides by arenesulphonyl tetrazolides[4,5] can be accounted for most probably by the fact that tetrazole, catalysing the second phase of the process, is produced in the first phase. Similar kinetic curves, involving the formation of up to 90% of the pyrophosphate in the first phase, have been obtained also for all the other catalysts enumerated.[17]

In order to establish the role of pyridine in the stage involving the formation of the phosphotriester from the pyrophosphate, the latter was obtained in the form of a solution in methylene chloride from (ClC_6H_4)pT(Ac) in the presence of TPS and (Tr)T as the OH-component. In the absence of pyridine, the reaction stops at this point; the addition of pyridine or γ-picoline leads to the formation of the dinucleoside phosphate. On the other hand, the addition of benzo-1,4-diazabicyclo[2.2.2]octene, whose $pK_a = 5.6$ and is close to that of pyridine, does not lead to the synthesis of the phosphotriester, which shows that in the given stage pyridine plays primarily the role of a nucleophilic catalyst.[43,56]

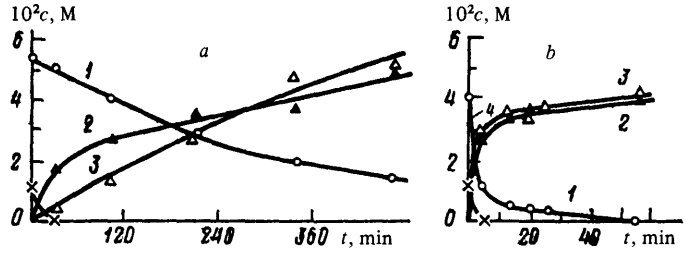
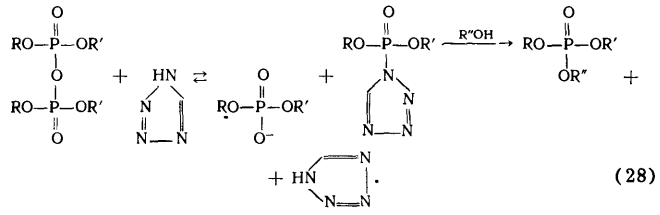


Figure 11. Kinetic curves for the reactions at 30 °C in pyridine; *a*) reaction of 0.05 M tetraphenyl pyrophosphate and 0.01 M diphenyl phosphorochloridate with 0.11 M (Tr)T; *b*) reaction of 0.04 M tetraphenyl pyrophosphate and 0.01 M diphenyl phosphorochloridate with 0.12 M (Tr)T in the presence of 0.25 M tetrazole; *1*) tetraphenyl pyrophosphate; *2*) the phosphotriester (Tr)TOP(O)$(OPh)_2$; *3*) diphenyl phosphoric acid; *4*) diphenyl phosphorochloridate.[41]

The catalytic role of tetrazole has been demonstrated in relation to the model reaction of tetraphenyl pyrophosphate with (Tr)T.[41] In order to rule out the possible influence of the condensing agent, tetraphenyl pyrophosphate was obtained by the reaction of diphenyl phosphoric acid with diphenyl phosphorochloridate. A small excess of the latter ensured the absence of undesirable traces of moisture from the system. After the addition of (Tr)T, diphenyl phosphorochloridate disappears in the course of several minutes and a gradual conversion of the pyrophosphate into diphenyl phosphate and the phosphotriester (Tr)Tp$(OC_6H_5)_2$ is observed (Fig.11*a*). The addition of tetrazole simultaneously with (Tr)T leads to the acceleration of the process by a large factor (Fig.11*b*); the reaction is completed in less than half an hour instead of several hours. If triethylamine is added simultaneously with tetrazole, the reaction is completed faster than it is possible to record the ^{31}P NMR spectrum, i.e. in less than 1–2 min. The diphenyl phosphotetrazolide signal is not recorded in either case, in agreement with the rapid interaction of this compound with the OH-component noted in

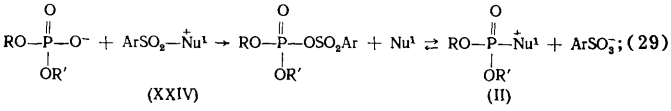
Section (III). Overall, the transformation of the pyrophosphate into the phosphotriester in the presence of tetrazole can be represented by the following scheme:



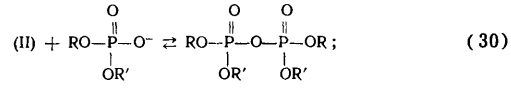
(28)

The equilibrium in the first stage of reaction (28) is greatly displaced to the left, because the addition of tetrazole to a pyrophosphate solution does not result in the appearance of a signal due to the tetrazolide of the phosphodiester in the ^{31}P NMR spectrum. The presence of a strong base should shift the equilibrium to the right (the proton is bound), which may account for the sharp acceleration of the interaction of tetraphenyl pyrophosphate with (Tr)T in the presence of tetrazole following the addition of triethylamine. However, the second stage also contributes to the acceleration of the process and this stage is likewise accelerated by triethylamine, as stated in Section III.

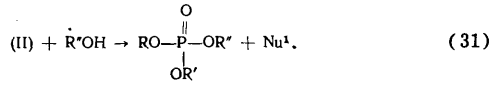
Taking into account the foregoing, including the fact that the $ArSO_2\overset{+}{N}\swarrow$ derivative of the condensing agent and not the condensing agent itself interacts with the initial phosphodiester, the overall mechanism of the phosphotriester condensation in the presence of TPS and pyridine or an analogous catalyst can be formulated as follows:



(29)



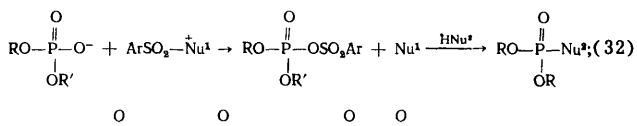
(30)



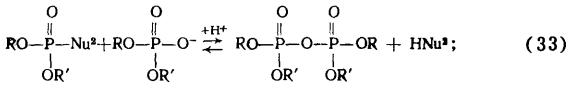
(31)

In the first phase of the reaction, the species (II) react preferentially via pathway (30), which leads to the accumulation of the pyrophosphotetraester. As the initial phosphodiester is consumed, the process is switched to pathway (31) to an increasing extent. Presumably in the second phase of the reaction, where reaction (30) is reversed as a result of the sharp decrease of the concentration of the phosphodiester, the main bulk of the product is formed via reactions (29) and (31).

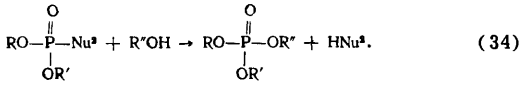
An analogous scheme can also be formulated for catalysis by tetrazole or nitrotriazole:



(32)



(33)



(34)

Since it is sufficient to have catalysts of the "pyridine" type for the occurence of the first phase of the reaction, including the formation of the derivative (XXIV), in phosphotriester condensations pyridine can be fully replaced by *N*-methylimidazole, while acetonitrile, dioxan, and many halogeno-hydrocarbons can be used as solvents.[10,15-18]

In contrast to this, tetrazole cannot convert the arenesulphonyl chloride into an active derivative of type (XXIV). In order that the reaction of the arenesulphonyl chloride with tetrazole, leading to the formation of the arenesulphonyl tetrazolide, should occur, a strong base must be present; in pyridine such interaction does not take place under the conditions of the phosphotriester condensation.[6] At the same time, as stated in Section (II), strongly basic amines prevent the formation of the mixed anhydride (VI) from arenesulphonyl tetrazolides and the phosphodiester. In catalysis of the phosphotriester condensation by tetrazole and nitrotriazole, pyridine, which is essential for the formation of compound (XXIV), must therefore be used as the solvent. Furthermore, pyridine is involved as a base in the reverse reaction (33) and reaction (34).[43]

It is noteworthy that, whereas the pyrophosphotetraester behaves as a typical intermediate in terms of the character of the kinetic curves (Figs.9 and 20), it is strictly speaking not an intermediate. Reactions (30) and (33) are not intermediate processes but constitute reversible side reactions. Their suppression can significantly accelerate the process. The question whether the pyrophosphotriester can be formed when the phosphotriester condensations are carried out on insoluble polymeric carriers, where the P-component is fixed on the carrier while the OH-component is in solution,[19,64-67] remains open.

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Functional Microanalysis by Chromato-spectrometric Methods

Ya.L.Kostyukovskii and D.B.Melamed

Chemical reactions involving the most important functional groups and yielding easily detectable compounds are discussed. The possible development of a system of functional microanalysis of organic compounds on the basis of chemical reactions, thin-layer and column liquid chromatography, and spectrometric methods is considered.
The bibliography contains 296 references.

CONTENTS

I. Introduction 199
II. Foundations of reactive chromato-spectrometric analysis 199
III. Methods of identifying organic compounds through functional groups 200
IV. Conclusions 208

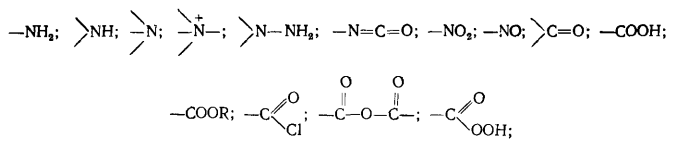
I. INTRODUCTION

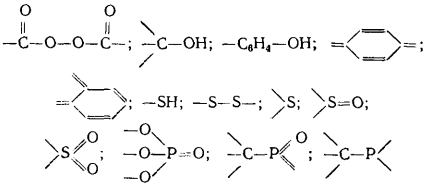
Analytical reactive chromatography includes chemical methods of preparing derivatives of the substances to be analysed, chromatographic separation, and detection of the derivatives. Reactive methods have greatly widened the scope of traditional chromatographic methods, and are now widely used in the analysis of organic compounds in the environment, in industrial and agricultural practice, in medicine, pharmacology, etc. Reactive chromatography is especially valuable for the determination of trace amounts of various substances in complex mixtures. It has also proved very successful as a method of functional analysis.

In recent years there have been two main trends in the development of organic functional analysis: the establishment of micro-methods of determining functional groups[1-3] and the application of these methods in conjunction with chromatographic separation.

Gas-chromatographic methods of functional analysis have been developed and reported most extensively.[4-6] On the other hand existing information on the combination of thin-layer chromatography (TLC) and column liquid chromatography with various methods of detection (in particular, spectrometric) has not yet been systematically reviewed, and the procedures have not been discussed as potential methods of functional analysis. The prospects of these methods are wider than those of gas-chromatographic methods, because they are applicable in principle not only to volatile compounds but also to involatile (and even to relatively unstable) compounds. The combination of chemical reactions (to produce easily detectable derivatives) and of the high resolving power offered by TLC and by column liquid chromatography, including detection by spectrometric methods, should provide an adequate foundation for a system of functional analysis of organic compounds in amounts of a few nanograms.

In this review we shall examine the chemical reactions used to prepare derivatives of the most important functional groups found in organic compounds:





and we shall generalise the most important results of recent work on the determination of the derivatives by a combination of TLC (or column liquid chromatography) and mass spectrometry, u.v. and visible spectrometry, and spectrofluorimetry.

II. FOUNDATIONS OF REACTIVE CHROMATO-SPECTROMETRIC ANALYSIS

Many chemical reactions have been used to convert the substances to be analysed into easily separable and detectable derivatives. Most of these studies have been directed towards reactive column chromatography. Their main outcome has been the identification of the optimum conditions for the synthesis of derivatives of organic compounds of various classes. The chemical reactions used for the functional analysis in conjunction with chromato-spectrometric methods can be applied either before the chromatographic separation (in order to convert the functional groups of the substances to be analysed into more easily separable and detectable derivatives), or after the separation (in order to reveal the functional groups).

The chosen chemical reactions should be selective towards the various functional groups, but in practice this requirement is not always met. Therefore in the analysis of complex samples a more reliable identification is obtained by using more than one reaction.

Two main schemes can be used for the analysis: 1) preparation of the derivatives, followed by chromatographic separation and spectrometric determination, and 2) chromatographic separation followed by chemical reaction and spectrometric determination. Depending on the chosen path, different requirements are specified for the reactions. In the analysis by the first scheme the derivatives are prepared by using reagents which give stable, easily separable, and

easily detectable products in almost quantitative yield.[7-10] Chromatospectrometric methods are often used with derivatives which absorb strongly in the u.v. and visible regions of the spectrum. Mass spectrometry, a powerful method of identification, can be used in principle to determine any derivative, but in practice the method is most successful with substances which form a large number of molecular ions and of characteristic fission ions.[11-15,19-21]

The derivatives are usually prepared outside the chromatographic assembly, but in some cases they have been prepared directly on the plate (for TLC) or in the liquid chromatograph, using fast reactions. Derivatives of multifunctional compounds are prepared by reactions at one or more groups: preferably the latter, since this improves the selectivity of the chromatospectrometric method. The preparation of derivatives from the substances to be analysed before carrying out the separation by liquid chromatography is often very effective, because it assists not only the separation and detection but also the interpretation of the results, thus greatly enhancing the reliability of the analysis.

In the second scheme the substance to be analysed is chromatographed first, and then the components are identified on plates or in eluates after being converted into easily detectable compounds by various chemical reactions. The choice of reactions for making visible the compounds on the TLC plates is relatively simple, but more stringent requirements apply to the reagents used in liquid chromatographs: the reaction must be fast, especially if used in a continuous process, and the excess of reagent should not interfere with the detection.[7,9,10] Many new models of liquid chromatographs are fitted with reactors for the preparation of easily detectable compounds.[7,9,10,16] The separation before the preparation of derivatives should be done under chromatographic conditions compatible with the properties of the functional groups of the substances to be analysed. Thus ion-exchange chromatography or reversed phase chromatography with ion pairing[7,10,17,18] are often used with acidic or basic compounds.

The most reliable method of identifying the separated components or their derivatives is mass spectrometry.[11,19-21] After separation of the mixture by TLC or column liquid chromatography the eluates of the various fractions are concentrated before being injected into the mass spectrometer. The more advanced systems offer a combination of a gas chromatograph, a mass spectrometer, and a computer. Some recently developed systems have even wider analytical capabilities, and include a liquid chromatograph, a mass spectrometer, and a computer.[11,20,22] However, so far these systems have been used only in development work, or to confirm the results of other analytical methods. More often the functional groups of the separated components are identified by u.v. spectrophotometry or spectrofluorimetry, or (in the case of TLC) by visual methods or with the help of a densitometer or other similar device.[7,9,10,18,23] In complex systems detection at two or more wavelengths has been recommended[24,25] as an alternative to recording the full absorption or fluorescence spectrum.

Chromato-spectrometric methods offer a very high sensitivity: the detection limit is 10^{-9}–10^{-12} g for mass spectrometers and fluorimeters (10^{-20} g if a laser is used), 10^{-8}–10^{-9} g for u.v. spectrophotometers, and 10^{-5}–10^{-7} g for visual assessment of the colour.

The quantitative determination of the identified substances is carried out by conventional chromatographic and spectrometric methods.[7,9,11,18,23,24,26,27]

The success of chromato-spectrometric methods of analysis is largely determined by the care taken in sample preparation, which is a difficult and critical stage of the process, especially in the determination of trace amounts of compounds in real samples from the environment, biological materials, food products, etc. This is because of the need to extract the trace impurities from a complex mixture in which the concentration of the wanted components is many times smaller than that of the other components.

A detailed discussion of methods of preparation and preliminary examination of samples for analysis is beyond the scope of the present review. Some relevant data are collected in Refs. 7 and 28–32. We shall only mention some of the more important details which we consider essential to a successful chromato-spectrometric analysis. An important aid to the extraction of substances for analysis is the use of mixed solvents of different polarity, and also of mixtures of counterions, which facilitate the removal of polar organic compounds. Reversed phase, ion-exchange, and gel permeation chromatography methods are also of interest.[7,9,11,28-30] Various forms of micro-distillation (especially under reduced pressure) from media at a suitable pH can also be used in the separation of volatile substances.[7,9,29,30,32] Extreme purification is usually laborious, and can lead to loss of material, for which allowance should be made when choosing a suitable method of analysis. By using chromato-spectrometric methods, involving a preliminary conversion of the compounds into their derivatives, the extract purification procedure can often be greatly simplified.[8-10,27,30] The reproducibility of the process can be improved by simultaneous analyses of experimental and of control samples prepared from the experimental samples by removing the compounds for analysis.[30,33]

A very important precaution is a preliminary study of the effect of acids, alkalis, oxidisers, and temperature on the substances for analysis, and also an elemental analysis and a determination of the spectral characteristics.[3,13,34] Often the compounds are available only in small quantities, insufficient for a detailed preliminary study. However, it is essential to obtain as much information as possible on the nature of the substances for analysis during the preparation and preliminary examination of the sample.

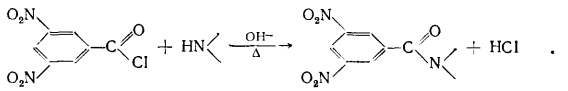
III. METHODS OF IDENTIFYING ORGANIC COMPOUNDS THROUGH FUNCTIONAL GROUPS

The success of the chromato-spectrometric methods of functional analysis depends on the quality of the chromatographic separation. In the determination of low-molecular-weight compounds in complex mixtures better results are obtained by chromatographing the derivatives. For example, in mass spectrometry the analysis of the derivatives is more effective than the analysis of the compounds themselves.[11-13,15,20,21] Many reagents for the various functional groups have been proposed: they all contain a fairly large group of aromatic or heterocyclic fragments which enhance the absorption of the molecule in visible and u.v. light or produce fluorescence. The "screened" functional groups can be identified after suitable chemical treatment (for example, hydrolysis). Compounds which are efficiently separated by TLC and column liquid chromatography methods are often analysed directly.

1. The $-NH_2$ and $>NH$ Groups

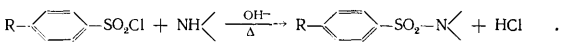
Many reagents and reactions for preparing derivatives of primary and secondary amines have been suggested. Acylation reactions are most frequently used, often at high temperatures and in the presence of catalysts (inorganic bases, tertiary amines, crown ethers, etc.). The most commonly used acylating agents are the acid halides of aromatic carboxylic acids and sulphonic acids.

Derivatives which absorb strongly in the u.v. are obtained by using 4-nitro-, 3,5-dinitro, 4-methoxy-, 4-dimethylamino-, 4-dimethylamino-3,5,-dinitrobenzoyl chlorides, and also 4-biphenyl-, 4-(4′-nitrophenylazo)benzene-, 4-(4′-dimethylaminophenylazo)benzenecarbonyl chlorides, etc.[7,8,10,14,35] The reactions follow the general scheme



Usually the yield is almost quantitative and the resulting amides are stable, easily extracted by organic solvents, and have an absorption coefficient in the u.v. region of about 14 000.[8,10,14] Mixtures of amides are easily separated by TLC or by column liquid chromatography. Many stationary phases and solvent systems have been used for these separations. Visual detection, and detection by mass spectrometry, can be used as well as u.v. spectrometry.[8,9,14,18,21,23,26,29,35,36] The sensitivity of detection of di- and polynitrobenzamides can be enhanced by treatment with alkali and acetone (Yanovskii reaction), which gives strongly coloured compounds.[38]

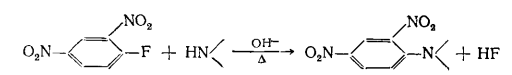
Derivatives which absorb strongly in the u.v. are obtained from the acid halides of aromatic sulphonic acids: 4-methyl-, 4-iodo-, 4-dimethylamino-, 4-(phenylazo)-, 4-(4′-*N*,*N*-dimethylaminophenylazo)benzenesulphonyl chloride, etc.[8,10,14,21] The reaction scheme is



Substituted sulphonamides are formed also by the reaction with trinitrobenzenesulphonic acid.[37,39] As a rule the sulphonamides absorb less strongly than the corresponding benzamides in the u.v.[10]

Compounds containing $-NH_2$ and NH groups form derivatives when treated with 1-dialkyl(C_1–C_5)aminonaphthalene-5-sulphonyl chlorides, *N*-methyl-2-anilinonaphthalene-6-sulphonyl chloride (mansyl chloride), 2-*p*-chlorosulphophenyl-3-phenylindone (disyl chloride), 4-(1-oxy-3-phenylinden-2-yl)benzenesulphonyl chloride, and 1,3-naphthoylenebenzimidazole-6-sulphonyl chloride.[7,10,14,27,40] Mixtures of sulphonamides are separated by TLC and column liquid chromatography methods, using a variety of stationary phases and eluents, and are detected by fluorescence, visual colour, u.v. absorption, and mass-spectrometrically.[14,18,26,27,36,41–43] Reactions with 1-dimethylaminonaphthalene-5-sulphonyl chloride (dansyl chloride) are widely used to identify primary and secondary amines, aminoacids (AA), aminophenols, and phenols.[10,14,27,44] We have shown that dansyl chloride can also be used to determine unsaturated amines.[44] The main advantage of dansylamides over other sulphonamides is the ease of separation and identification of the derivatives. Recommended conditions for the determination of dansylamides are given in Refs.12, 14, 18, 21, 27, 42, 43, and 45.

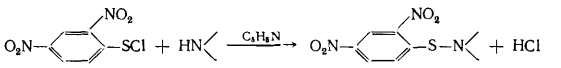
Other compounds including a relatively mobile halogen atom are also used to prepare derivatives, in particular 2,4-dinitrofluorobenzene, 2,4-dinitrochlorobenzene, 2,4-dinitro-5-fluoroaniline, 7-fluoro- and 7-chloro-4-nitrobenzo-2-oxa-1,3-diazole (NBD chloride), and others.[8,10,14,15,33,46,47] 2,4-Dinitrofluorobenzene has been most widely used in practice, because it forms derivatives which absorb strongly in the u.v. and are easily separated under a variety of chromatographic conditions:



The analytical results have been confirmed by mass spectrometry.[8,14,26,37,48]

NBD chloride, which forms fluorescent NBD amides also absorbing strongly in the visible and u.v. spectra,[8,14,33,49,50] has been used almost as widely. Various amines and aminoacids give coloured derivatives (yellow, orange, or red) which can be used as an additional identifying criterion.[33,49,50] NBD–amine mixtures are easily separated by TLC and column liquid chromatography, and identified by fluorescence, colour, light absorption in the u.v., and mass spectrometry.[15,26,33,51–55] We have shown that NBD chloride is superior to dansyl chloride in a number of characteristics, including selectivity of the determination and stability of the derivatives.[27,55]

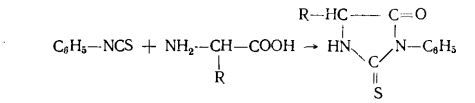
Another compound with a mobile halogen atom is 2,4-dinitrobenzoylsulphenyl chloride, which forms derivatives which absorb in the u.v.:



These derivatives are separated by TLC, for example on silica gel or Siluphol in the benzene–cyclohexane–chloroform–ethanol system.[35,36]

Other reagents have been suggested for preparing derivatives from $-NH_2$ and $>$NH groups, but they are used far less often.[8,57,58] They include 9-fluorenylmethylchloroformate, which gives fluorescent compounds, and *N*-(chloromethyl)phthalimide and *N*-(chloromethyl)isatin, which give products with a strong u.v. absorption.

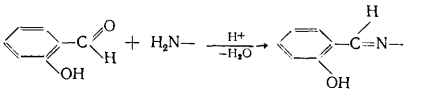
The large group of substituted iso- and isothiocyanates forms derivatives with amines. They include phenyl- and 4-(6-methylbenzothiazol-2-yl)phenyl isothiocyanates, phenyl-, naphthyl-, and 4-phenylazobenzoyl thiocyanates, etc.[7,8,18,21,34,35] These are most commonly used to identify aminoacids by forming thiohydantoins:



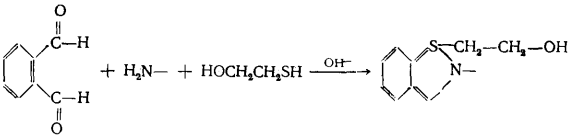
These compounds are readily separated by TLC and column liquid chromatography methods, and determined by u.v. absorption. Analytical results have been confirmed mass spectrometrically.[10,26,59–61]

Amino groups can also be identified by the formation of fluorescent compounds with fluorescein-, 9-acridyl-, and 4-dimethylamino-1-naphthalyl isothiocyanates or with 4-(6-methylbenzothiazole-2-yl)phenyl isocyanate or 2-(4-isothiocyanatophenyl)-3-phenylindone.[7,10,14,27,62]

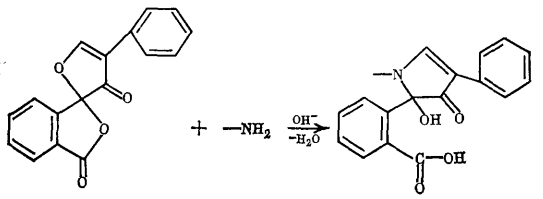
Amines (especially the primary) react vigorously with reagents containing a carbonyl group, for example with 4-dimethylamino- and 2,4-dinitrobenzaldehydes, or with salicylaldehyde:[8,35,38]



The resulting azomethynes react with diphenylboric anhydride to give complexes easily separated by TLC.[10,63] *o*-Phthalic aldehyde (*o*-PA) has been used frequently: in the presence of some thio-compounds (for example, monothioglycol) it forms fluorescent cyclic compounds which can be separated chromatographically:[10,27,51,64–67]



The identification of primary amino groups and AA with 4-phenyl-*spiro* (furan-2,3H-1-phthalan)-3,3'-dione (fluram)[10,14,27,35,68,69] is also of interest:



The resulting, strongly fluorescent compounds are easily separated by TLC or column liquid chromatography.[10,14,27,35,68,69]

Fluram and *o*-PA can be used as reagents for the derivatisation of secondary amines after conversion into primary amines, for example by treatment with NaOCl and 2,2'-thiodiglycol.†

Chromato-spectrometric methods of functional analysis can be applied to compounds in which $-NH_2$ or $>NH$ groups can be produced by appropriate chemical reactions. They include pesticides, therapeutic products, and toxic and carcinogenic compounds.[7,9,10,18,27,30,54] For example, methods of converting carcinogenic nitrosamines into the corresponding secondary amines and identifying the latter as dansyl amides or NBD amides have been developed.[33,42,49,55] These derivatives have been used in the detection of nitrosamines in the environment by combined chromatographic and mass spectrometric analysis.[15,45,55,70]

Chromatographic separation before derivatisation is preferred in the functional analysis of AA and aromatic or heterocyclic amines. TLC of aminoacids is usually carried out on silica gel, aluminium oxide, cellulose, polyamides, or ion-exchange resins (for example, Fixion or Dowex) in various systems containing phenols, organic acids, and ammonia.[23,26,50,71-76] Some aliphatic amines and AA are well separated by high-performance TLC methods on chemically bonded phases of the RP-18 type.[73,77,78]

Aromatic amines are separated on a thin layer of silica gel, alumina, polyamide, cellulose, and also on ion-exchange resins and on silica gel impregnated with phenols, oxalates, acetates, sulphates, chlorides, and surface-active substances, using different solvent systems.[23,26,71-74,79,80] A study of the dependence of the chromatographic mobility of amines on their structure has been reported.[26,79]

Various reagents have been suggested for the visualisation of compounds containing $-NH_2$ and $>NH$ groups, both universal (iodine, $KMnO_4$, $K_2Cr_2O_7$, phosphomolybdic and phosphotungstic acids, H_2SO_4, $SbCl_3$, $SbCl_5$, pH indicators, etc.) and relatively specific in action. The latter include solutions of ninhydrin, fluram, *o*-PA, NBD chloride, $Ca(OCl)_2$ in conjunction with KI, a mixture of acetylacetone and formaldehyde, etc.[14,26,27,53,73-75,78]

Aromatic amines can also be determined by the following reactions: coupling with diazotised sulphanilic acid, 4-nitroaniline, etc., diazotisation and coupling with phenols (say), or treatment with 4-dimethylaminobenzoic and cinnamaldehyde. U.v. spectrophotometry is used for detection.[18,26,38,71,78,81] Some aromatic and heterocyclic amines show spontaneous fluorescence.[53,82]

Ion-exchange liquid chromatography has been used most commonly in the separation of AA, but also (on a few occasions) for aliphatic amines. The great importance of AA in biology has stimulated the development of automatic and semi-automatic AA analysers, which can be used also to determine some other amino compounds (mono-, di-, and polyamines#). The most commonly used stationary phases include Amberlites, Apinexes, Biorex, Sephadexes, Partisil SCX, etc.; various buffer systems are used as eluents. The eluates are treated with ninhydrin, *o*-PA, fluram, NBD chloride, or other developers, and their colour is noted visually or measured spectrophotometrically or spectrofluorimetrically.[9,10,27,83-85] The high-performance liquid chromatography method (usually in the reversed-phase mode) is now often used in the analysis of AA and aliphatic amines on Lichrosorb RP-18, Permaphase ODS, Sorbax C_8 or ODS, μ-Bondapak C_{18}, and other stationary phases with aqueous-alcoholic mixtures often containing counter-ions: the addition of counter-ions has been shown to improve the separation of AA.[10,17,18,76,85-90] The separated compounds are usually derivatised with ninhydrin or *o*-PA, and the resulting derivatives are determined using u.v. or fluorescence detectors.§

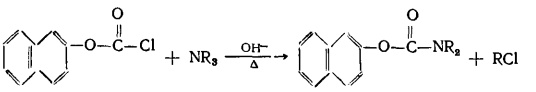
Extensive studies of the separation of aromatic amines by high-performance liquid chromatography have been reported. Various stationary phases and eluents have been proposed, and u.v. detectors have been used to identify the amines.[7,10,81,91-94] Mass spectrometric methods have also been used for detecting aromatic amines after their separation.[13,20,95,96]

Amides are usually analysed after being converted into the corresponding amines. In principle the formation of hydroxamic acids could be used to detect the amides after separation.[23,38]

The very large number of chemical reactions proposed for the derivatisation of primary and secondary amines allows an easy choice of the best variant for the separation of particular systems. It is often convenient to prepare fluorescent derivatives and separate them by TLC: a simple method, which offers a high sensitivity in the identification of these functional groups.

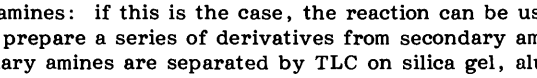
2. The N and $>\overset{+}{N}$ GROUPS

The chromato-spectrometric analysis of these groups has not yet been adequately developed. Some tertiary amines have been determined through their derivatives formed by the reaction with pentafluorobenzyl- or 2-naphthylchloroformate:[10,97]



A likely intermediate step in this reaction is the dealkylation of the amines: if this is the case, the reaction can be used also to prepare a series of derivatives from secondary amines.

Tertiary amines are separated by TLC on silica gel, aluminium oxide, or other sorbents. The solvent systems usually contain ammonia and dichloroethane. The separated compounds are made visible by the Dragendorf reagent, K_2PtCl_6, chloranil, tetranitromethane, tetracyanoquinonedimethane, tetracyanoethylene, etc.[2,3,14,26,98,99] With tetracyanoethylene the reaction is



†see A.Himuro, Analyt.Chim.Acta, 1983, 147, 317.

#see N.Sauem and E.Ronald, J.Chromatogr., 1983, 256, 313.

§see R.Cunico and T.Schlabach, J.Chromatogr., 1983, 266, 461; R.Simpson, J.Chromatogr., 1983, 261, 407.

The separation of tertiary amines by high-performance liquid chromatography relies on the use of mobile phases containing counter-ions, for example 9,10-dimethoxyanthracene-2-sulphonate or acridone-2-sulphonate.[9,10,18,100,101]

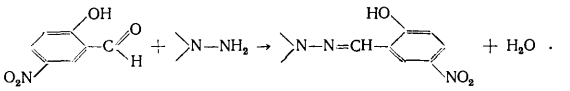
Compounds containing the $\geqslant\overset{+}{N}-$ group are separated by TLC on silica gel, aluminium oxide, or cellulose, with mobile phases usually containing hydrochloric, acetic, citric, or other acids. Visualisation is carried out by treating the plate with Dragendorf's reagent or with K_2PtCl_6.[3,23,102-104]

Quaternary ammonium compounds are chromatographed on ion-exchange resins, for example Partisil SCX, Amberlite CG-50, or Zeokart 226, with eluents containing counter-ions of the naphthalene- or anthracene-2-sulphonate type.[9,85,105-107]

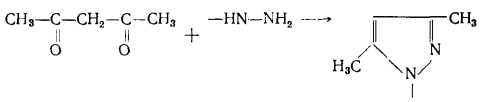
Efficient separation of these substances, including long-chain compounds, is achieved by the high-performance liquid chromatography method on Nucleosil-5 $N(CH_3)_2$, using the hexane–chloroform–ethyl acetate system as the solvent, or on Nucleosil CN with an aqueous solution of methanol containing *p*-toluenesulphonic acid.¶

3. The $\geqslant N-NH_2$ Group

Compounds containing this group (alkyl- and arylhydrazines, acid hydrazides, etc.) can be analysed chromatospectrometrically by preparing relatively stable and easily separable compounds. Thus, hydrazines react with 5-nitro-2-hydroxybenzaldehyde to give[8,10,21,38]



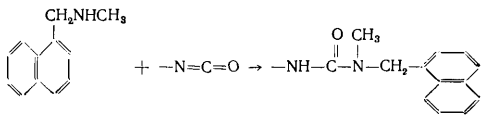
Alkylhydrazines react with acetylacetone to give pyrazolone derivatives:[8,10,21]



The fast reaction of the $\geqslant N-NH_2$ group with carbonyl compounds can be used to identify this group by using aldehydes and ketones. The hydrazines are usually separated (before derivatisation) by high-performance liquid chromatography on phases of the μ-Bondapak C_{18} or Aminex type, with various eluents.[18,108,109]

4. The −N=C=O Group

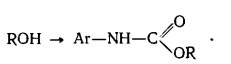
As was said above, isocyanates are used to form derivatives with amines: the same reaction can be used to identify the isocyanates. 9-(*N*-methylaminomethyl)anthracene or *N*-methyl-1-naphthalenemethylamine are most often used:[110,111]



Other reagents for isocyanates include *N*-4-nitrobenzyl-*N*-alkylamines, aminophenols, 1-(2-pyridyl)- and 1-(2-methoxyphenyl)piperazines, which form derivatives with a strong u.v. absorption.[112-116]

¶ see M.Kudon, J.Chromatogr., 1983, **261**, 293.

Aromatic isocyanates react with alcohols by the scheme



The derivatives are easily separated chromatographically, and identified by u.v. spectrometry.[110,112-116]

The −N=C=O group can be detected after separation (for example, by high-performance liquid chromatography on μ-Bondapak C_{18} or Lichrosorb RP-18, using mobile phases of aqueous acetonitrile or methanol): detection in this case is by u.v. or i.r. spectroscopy.[2,10,21]

Isocyanates (and also isothiocyanates) can also be identified chromato-spectrometrically after hydrolysis to the corresponding amines.

5. The $-NO_2$ and −NO Groups

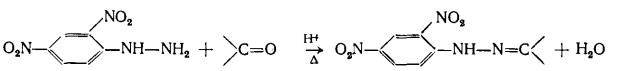
Chromato-spectrometric methods relying on a preliminary separation by TLC or high-performance TLC on RP-2 or RP-18 silica gel, acetylcellulose, etc. have been applied to the analysis of nitrocompounds. The solvent systems usually include methanol, ethanol, and acetonitrile.[26,117,120] The presence of the NO_2 group causes a fairly strong u.v. absorption, which can be used for detecting the nitro compounds on chromatographic plates or in eluates.

Aromatic di- and polynitro compounds can be made visible by the Yanovskii reaction, or by treating them with *N*,*N*-diethylaniline or Na_2SO_4.[117-119] Nitro compounds are separated, for example, by reversed phase liquid chromatography on Lichrosorb RP-18 or RP-8, using aqueous solutions of alcohol or of acetonitrile as the mobile phase. U.v. detectors are used for their identification.[91,120,121] Analytical results have been confirmed mass-spectrometrically.[122,123]

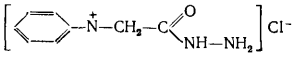
A few studies of the identification of the NO group by chromato-spectrometric methods have been reported. Various *N*-nitrosamines have been determined (after denitrosation) through the resulting nitrite ion and amino group.[33,42,55] Nitroso compounds can be converted into nitro compounds or into hydrazines by oxidising or reducing treatment respectively.

6. The $\geqslant C=O$ Group

Most of the work on the preparation of derivatives of carbonyl compounds has been on the reaction with hydrazines (in particular, phenylhydrazine and its derivatives):[8-10,21,35,124]



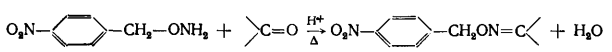
Similar reactions are obtained with azobenzene-4-carboxyhydrazine and with the Girard reagent:[10,35]



By using dansyl-, mansyl-, and NBD-hydrazines, 2-phenylacetyl-1,3-indandione-1-hydrazine, isonicotinylhydrazine, or other compounds, strongly fluorescent hydrazones have been obtained.[7,10,21,54,125,126] Silica gel, aluminium oxide, and cellulose can be used as sorbents for the TLC of hydrazones.[3,26,127,128] These compounds are detected by their colour, by fluorescence, or by u.v. absorption.[26,124,126-128] Hydrazones have also been separated by high-performance liquid chromatography and identified by u.v. or fluorescence detection.[10,

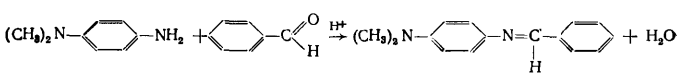
[126, 129–133] Good results were obtained, for example, by using Sorbax ODS and a mixture of acetonitrile and water.†

Derivatives of carbonyl compounds which absorb in the u.v. are obtained by condensation with substituted hydroxylamines and semicarbazides, for example with 4-nitrobenzyloxyamine:[10, 13, 21]



The conditions for the chromatographic separation of oximes and semicarbazones have been discussed.[9, 21, 26, 35, 134, 135] The mass spectra of many hydrazones and oximes give a convenient identification of these compounds.[10, 21, 126, 134, 136]

Aldehydes react easily with primary amines, for example with *N*,*N*-dimethyl amino-1,4-, 1,3-, and 1,2-phenylenediamine, ethylenediamine, aminopiperidine, etc.[8, 35, 124, 137] These reagents are useful in practice for the functional analysis of aldehydes because the resulting Schiff's bases are strongly coloured and absorb in the u.v. region of the spectrum. Aromatic aldehydes react as follows:



α-Dicarbonyl compounds and α-keto-acids form fluorescent quinoxazolones with 1,2-phenylenediamine.[8, 136–140] Both the Schiff's bases and the quinoxazolones are easily separated by chromatographic methods.[35, 137–140] Aldehydes (unlike ketones) react with 5,5-dimethylhydroresorcinol (dimedon) to give coloured compounds which can be separated by TLC.[13, 35, 141, 142] The α-oxomethylene group is identified by the formation of fluorescent compounds by the reaction with *N*-methylnicotinamide chloride. The products are separated by thin-layer or column chromatography.[9, 10, 143] Aliphatic aldehydes form fluorescent lutidines by reacting with acetylacetone and primary amines.[26, 27, 53, 144]

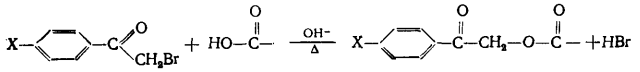
Substances containing a carbonyl group can be separated before derivatisation by TLC on silica gel, alumina, or cellulose, usually with a system of solvents of widely different polarities. Visualisation by universal or by relatively specific reagents is possible (for example, *o*-aminobiphenyl or other aromatic amines).[26, 32, 135, 145]

Good results have been obtained in the separation of carbonyl compounds by normal or reversed phase liquid chromatography on various stationary phases. Detection was by u.v. absorption or, after treating the eluent with *o*-phenylphenol, *N*-methylnicotinamide chloride, etc., by a fluorescence detector.[9, 131, 135, 143, 146, 147] The results have been confirmed mass spectrometrically.[11, 13, 136, 148]

Substances containing the >C=O group are often determined by derivatisation followed by detection in the u.v. or visually (by colour). Fluorescent derivatives are very seldom used in spite of the much higher sensitivity which they offer. This may be due to the difficulty of preparing the necessary reagents.

7. The –COOH and –COOR Groups

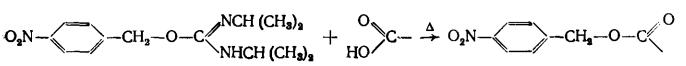
Derivatives of carboxylic acids are often prepared from phenacyl halides, for example 4-bromo-, 4-methoxy-, 4-nitro-, or 4-phenylazo-*N*,*N*-dimethylaminobenzeneazophenacyl bromides:



†see S.Slavin, J.Liq.Chromatogr., 1983, **6**, 425.

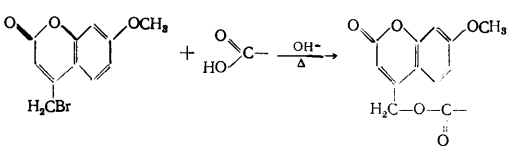
Phenacyl esters absorb strongly in the u.v. (absorption coefficient ~18 000),[7–9, 10, 35, 135, 149, 150] and naphthacyl esters, formed from compounds with a carboxylate group by the action of 2-naphthacyl bromide or 1-bromoacetylpyrene, are fluorescent.[10, 151, 152] TLC of these derivatives is carried out on silica gel (Lichrosorb RP-18) in various solvent systems (benzene–ethyl acetate, dimethylformamide–water, etc.).[26, 135, 150, 153] Separation is by liquid chromatography, for example in the reversed phase mode on μ-Bondapak C_{18}, μ-Porasil C_{18}, Lichrosorb RP-18, or Radialpak AC_{18} by the gradient elution method. The compounds are detected by mass spectrometry or by using fluorescence or u.v. detectors.[151, 152, 154–160]

An interesting method of identification of carboxylic acid groups by u.v. spectrophotometry relies on converting the acids (including long-chain acids) into benzyl or nitrobenzyl esters. The reaction is carried out by using the appropriate bromides, or 4-nitrobenzyl-3-*p*-tolyltriazine, or *p*-nitrobenzyl-*N*,*N*'-diisopropylisourea:[7, 8, 10, 135, 149]



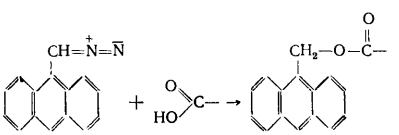
These esters are stable and easily separated by TLC or column chromatography on a variety of phases.[9, 18, 26, 135, 149]

Fluorescent esters, which are of interest for the identification of the carboxyl group, can be prepared by the reaction with chloromethylisatin or chloromethylanthracene, *N*-(chloromethyl)- or *N*-(chloromethyl-4-nitro)phthalimides, 4-bromomethyl-7,8-benzocoumarin, and 4-bromethyl-7-acetoxy- or 4-bromomethyl-7-methoxy coumarins.[8, 54, 58, 138, 161–166]



The conditions for separating these esters by various methods have been reported,[54, 162–168] including liquid chromatography on Partisil C_{18} or Nucleosil $10C_{18}$ with elution gradients in an aqueous methanol solution.

Fluorescent derivatives of acids are obtained also by the action of diphenyl-, 1-naphthyl-, 1-(4-biphenyl)-, or 9-anthryldiazomethanes:



The resulting compounds are separated by liquid chromatography (for example, in the reversed phase), using fluorescence or u.v. detection methods.[7, 169–172]

9-(Hydroxymethyl)anthracene, which forms fluorescent esters easily separable by chromatography, has been suggested[173] as a reagent for the carboxyl group.

The ability of carboxylic acids to react with amines (in particular, 1-naphthylamine, *p*-aminophenol, and 9,10-diaminophenanthrene) to give amides has also been used in practice.[174, 175] Separation was by liquid chromatography on μ-Bondapak C_{18} or Nucleosil C_{18}, with an aqueous solution of methanol as the eluent and fluorescence or u.v. detection. Compounds containing the –COOH and –COOR groups form

hydroxamic acids with hydroxylamine, which are easily separated and identified by their colorimetric reactions with tervalent iron.[1,2,26,38]

Derivatives obtained from polyfunctional compounds containing a carboxylic group have been discussed in many papers. Thus α-ketoacids react with 2,4-dinitrophenylhydrazine,[7-9,26,153,176] o-phenylenediamine,[8,10,138-140,177] and *N*-methylnicotinamide chloride.[9,10,143] Some hydroxyacids produce fluorescent compounds with resorcinol and 2-naphthol.[27,53,138]

Many publications discuss the chromatographic separation of substances containing −COOH and −COOR groups before derivatisation. Low-molecular-weight acids are separated by TLC on silica gel, alumina, polyamide, cellulose, starch, and other sorbents by using a system of solvents usually including alcohols, ethers, and bases (ammonia, diethylamine, etc.).[26,80,153,178-182] Long-chain acids are usually separated on silica gel impregnated with undecane or dodecane by using a system of solvents containing acetonitrile, dimethylformamide, and formic or acetic acid.[26,80,153] The thin-layer separation of esters of saturated carboxylic acids is carried out similarly.[26,153,180,183,184] Saturated acids are easily separated from unsaturated acids by TLC on silica gel impregnated with Ag^+.[18,26,182]

Silica gel or aluminium oxide with various solvent systems, often including methanol, formic and acetic acid, ammonia, etc. are used for the separation of aromatic acids.[26,80,185] The *p*-, *m*, and o-substituted aromatic acids are separated by TLC by using polyamide with aqueous solutions of α-cyclodextrins.[186]

Di- and polyacids are often separated on unmodified silica gel, but better results are obtained on silica gel or kieselguhr impregnated with poly(ethylene glycols), using solvent systems which include alcohols, tetrahydrofuran, formic or acetic acid, and ammonia.[3,26,153,188]

Many reagents have been proposed for determining the acids separated by TLC, but the universal reagents (iodine, pH indicators, phosphomolybdic acid, etc.) are still the most widely used.[26,153,178,180,184,185] Di- and polyacids form coloured complexes with Cu^{2+} salts, and fluorescent derivatives with dicyclohexylcarbodiimide.[187,188]

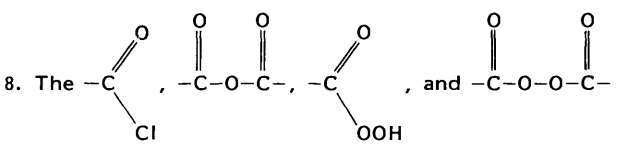
These acids are separated by reversed-phase (column) liquid chromatography, using counter-ions.[7,17,146,157,182,189-194] Other forms of chromatography have also been used (in particular, ion-exchange chromatography), and various analytical procedures have been recommended.[16,31,182,195-203]

The esters of saturated acids are usually separated by reversed-phase liquid chromatography, for example on Lichrosorb RP-18 or Bondapak C_{18}, using aqueous solutions of methanol or acetonitrile as the mobile phase.[9,18,182,194,204]

Unsaturated acids are chromatographed on Corasil P, Porasil A, Partisil 10 or 20, Spherisorb 5W, and other sorbents, containing 2–5% Ag^+. Silver nitrate is added also to the mobile phase by using aqueous organic solvents.[9,18,205-207]

The best conditions for the column liquid chromatography of polycarboxylic acids have been identified.[18,91,157,182,197,203] The visualisation of the acids after separation is usually straightforward: it relies on the absorption of the acids in the i.r. and near-u.v. regions of the spectrum, the absorption at the shorter wavelengths being the more effective for aromatic acids.[18,91,189,190,199,202,205,206,208] Some acids have been determined by treating the eluates with o-nitrophenol, Ce^{4+} salts, etc.[7-10,18,182] Complex samples have been successfully analysed by chromato-mass spectrometry, using column liquid chromatography for the separation stage.[11,13,136,148,209,210]

Thus both schemes of chromato-spectrometric analysis can be used to determine substances containing −COOH groups, depending on the properties of the sample.

8. The 

Groups

Anhydrides and acid chlorides are determined by the methods used for acids after converting them into the corresponding derivatives or into the acids. Some of these compounds form phenylmethane dyes when treated with *p*-dimethylaminobenzaldehyde and *N*,*N*-dimethylaniline on silica gel.[211]

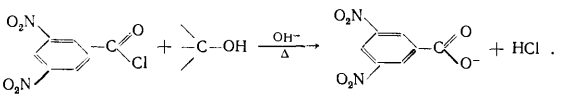
Hydroperoxides and peroxides can be identified after reduction to the acids. Chromato-spectrometric methods of analysis of these compounds have been proposed, even without derivatisation, by using normal or reversed-phase TLC in conjunction with detection by u.v. absorption.[18,26,212-215]

For example, the hydroperoxides of the linoleic acid isomers are well separated on Spherisorb Si 60 with the ethanol–hexane system.# The sensitivity of the analysis can be increased by adding sodium iodide or aromatic mono- and diamines to the eluent.[9,215,216]

The column liquid chromatography method has been applied[18] to hydroperoxides after converting them into ethers.

9. The $\geq$C–OH Group

The most extensive studies have been carried out on the reactions of alcohols with 4-methoxy-, 4-methylthio-, and 3,5-dinitrobenzoyl chlorides, by the scheme[2,7-10,32,35,135,217]

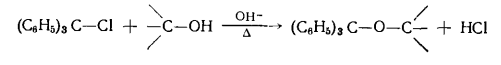


The resulting esters are more stable than the corresponding amides.

Coloured and strongly u.v.-absorbing esters (absorption coefficient ~14 000), suitable for the identification of the alcohols, are obtained by treating the sample with 4-(4′-nitrophenylazo)benzene- and 4-(4′-dimethylamino phenylazo)-benzenecarbonyl chlorides; separation is by TLC, usually on silica gel, and also on starch, cellulose, or talc, with various solvent systems.[26,32,218] Reversed-phase liquid chromatography on μ-Bondapak C_{18}, Lichrosorb RP-18, etc. has also been applied successfully to the separation of esters: elution was with aqueous solutions of alcohols, and detection by mass spectrometry or u.v. spectrophotometry.[7-10,135,219]

Sulphonyl chlorides (except 4-iodobenzenesulphonyl chloride and disyl chloride) are not often used to prepare alcohol derivatives. Disyl chloride forms strongly fluorescent esters.[9,21,40,220,221]

Alcohols also react with other compounds containing a relatively mobile halogen atom, for example with 2,4-dinitrofluorobenzene, 2,4-dinitrobenzenesulphene chloride, and triphenylchloromethane (trityl chloride).[2,35,135,222] In the latter case the reaction is

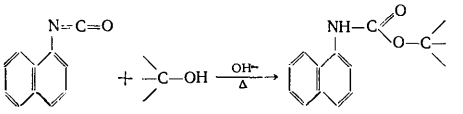


#see J.Koskas, J.Chromatogr., 1983, **258**, 2880.

We note that ethers of this type, unlike the corresponding amine derivatives, are insoluble in acids.[10]

Fluorescent derivatives, suitable for identification, are formed by primary alcohols with 1-ethoxy-4-(dichloro-5-triazinyl)naphthalene, which also contains mobile halogen.[7,10]

Stable esters which absorb u.v. radiation or fluoresce according to the choice of reagent have been obtained by the reaction of alcohols with isocyanates. The preparation of these derivatives with phenyl-, *o*-nitrophenyl-, *p*-toluenesulpho-, 1-naphthylanthranyl-, and 4-(6-methylbenzothiazol-2-yl)phenylisocyanates has been reported:[2,13,35,62,223]



These esters can be separated by TLC on silica gel, MNSilG, Lichrosorb RP-18, and other sorbents, with different solvent systems.[26,62,223,224] Satisfactory separation is obtained by reversed-phase column liquid chromatography on Lichrosorb RP-18 and silica gel C_{18} with gradient elution by mixtures of acetonitrile and methanol with water; determination is by fluorescence or u.v. detection.[9,35,62,223] The separation of these esters by normal-phase chromatography has also been reported.[9,18,225] An interesting analytical scheme[3,226] relies on the reaction of C_1–C_6 alcohols with hydrogen sulphide and potassium hydroxide to give alkyl xanthates, which can be separated in a thin layer of microcellulose with a butanol–water–ammonia eluent and identified by u.v. spectrophotometry.

Compounds containing the –CH(OH)–CH(OH)– group are identified by the formation of coloured cyclic derivatives with aldehydes and fluorescent derivatives with naphthalene- and phenanthreneboric acids.[177,227]

Many aliphatic alcohols are separated chromatographically by TLC before derivatisation. The sorbents for the separation of the lower alcohols are silica gel, aluminium oxide, or cellulose, and for the higher alcohols silica gel or kieselguhr impregnated with paraffin oil. In the latter case aqueous-organic solvent systems are used.

Glycols and polyhydric alcohols are chromatographed on silica gel impregnated with ammonium borate or on magnesium silicate, aluminium oxide, etc.[3,26,153,178,228] Visualisation of these alcohols after separation by TLC or column liquid chromatography is usually by universal reagents.[3,26,135,178,228] Selective reagents have also been used, including sodium metavanadate and 8-hydroxyquinoline, which form coloured derivatives.[2,26,135]

Substances containing the $\geq$C–OH group have been separated by reversed-phase column liquid chromatography on Partisil-5 ODS, Sorbax ODS, etc., with aqueous-organic eluents, and identified by using u.v. detectors.[16,18,138,147,229,230] Equally good results were obtained by normal-phase, ion-exchange, and other forms of chromatography.[231,232] Sephadex LH-20 has been used to separate short-chain from long-chain alcohols.[219,231]

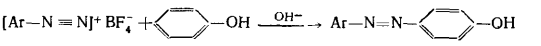
Polyhydric alcohols have been separated on Partisil A, Aminex A27, and other sorbents with various eluents, and identified by u.v. absorption or visually (by colour) after reaction with acidified $K_2Cr_2O_7$ solutions.[3,9,18,31] The determination of alcohols in eluates by a luminescence method with hydrogen peroxide and cobalt luminal has been reported.[233] In complex systems the presence of alcohols has been confirmed by mass spectrometry.[11,13,148]

Thus in the analysis of alcohols it is usually preferable to develop a colour or a derivative which absorbs in the u.v. before carrying out the chromatographic separation.

10. The $-C_6H_4-OH$ Groups

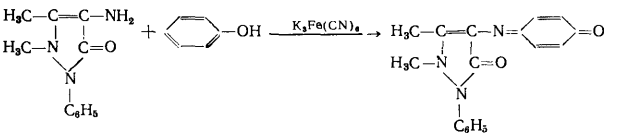
One of the most widely used methods of preparing derivatives of phenols and of alcohols is the reaction with substituted benzoyl chlorides, especially 4-nitro- and 3,5-dinitrobenzoyl chlorides.[2,9,10,18,32,35] Derivatives obtained by the reaction with the acid chlorides of sulphonic acids are also used to identify the phenyl groups. Thus 4-iodo- and 4-azobenzenesulphonyl chlorides give products which absorb in the u.v., while fluorescent products are obtained with dansyl and disyl chlorides.[7,9,27,35] Dansyl chloride is used most often, giving dansyl esters under conditions similar to those used in the preparation of dansylamides but at a higher pH. Polysubstituted derivatives are obtained from polyphenols and from aminophenols.[7,21,27,54,234] The products are separated either immediately after the reaction or after extraction and concentration by TLC or by high-performance TLC or column liquid chromatography, and are determined by u.v. absorption, fluorescence, or mass spectrometrically.[7,10,20,54,234] Chromato-spectrometric methods based on dansyl chloride are now widely applied in the analysis of various contaminants, therapeutic products, pesticides, and other compounds containing phenolic hydroxide or reacting to give phenols.[10,18,27,54,68]

Fluorescent or u.v.-absorbing derivatives recommended for determining phenols include the compounds with 2,4-dinitrofluoro- (or chloro-) benzene, *p*-(5-fluoro-2,4-dinitrophenylazo)-*N*,*N*-dimethylaniline, 1-ethoxy-4-(dichloro-5-triazinyl)-naphthalene, and others.[7–9,35,235] More specific derivatives, with u.v. absorption and colour, are formed by the reaction with diazonium salts:[2,3,38,236,237]



Diazonium salts prepared from 4-nitrobenzoic or sulphanilic acid or from 4-aminobenzonitrile are most often used in this reaction. The azophenols are efficiently separated by TLC on silica gel or by reversed- or normal-phase column chromatography (for example, on Lichrosorb RP-18 with an aqueous solution of methanol): detection is visual, by colour.[7,32,236–238]

Coloured quinoneimines are formed by the reaction of phenols with 4-aminoantipyrine:[2,3,32,38]



The separation of the quinoneimines is straightforward: either by TLC on silica gel or by reversed-phase of normal-phase column chromatography with photometric detection.[26,32,233,239] For example, complex mixtures of phenols can be separated as quinoneimines on μ-Bondapak C_{18} and on μ-Bondapak CN with an aqueous solution of methanol or a mixture of hexane and tetrahydrofuran as the mobile phase§.

The most interesting of the substances less frequently used for the determination of phenols is 1-nitroso-2-naphthol, which reacts with some substituted phenols to form fluorescent compounds easily separated chromatographically.[3,27,53]

The separation of phenol derivatives prepared directly on a chromatographic plate by treatment with a solution of Fast Blue BB has been reported.[240]

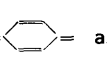
§see G.Blo, J.Chromatogr., 1983, 257, 69.

Many papers describe separations of phenols before derivatisation. The TLC of these materials is carried out on silica gel, RP-18 silica gel, or silica gel impregnated with polyamines or with vaseline, surface-active substances, or $AgNO_3$, and also on polyamide, cellulose, volcanic tuff, Dowex 50W, etc. Mixtures of organic solvents, buffer systems, and solutions of α-cyclodextrin are used as the mobile phase.[26,72,241-246]

Polybasic phenols are separated on silica gel or aluminium oxide with eluents which usually include chloroform and methanol.[26,247-249] After separation the phenols are made visible by treatment with universal reagents.[26,54,135,244,247] Coloured or fluorescent compounds are formed by treating the phenols with solutions of Ce^{4+}, Fe^{3+}, or Th^{4+} salts.[3,38,135,241] Diazonium and antipyrine salts (with $K_3Fe(CN)_6$) are more specific for phenols.[2,3,7,26,246] Polybasic phenols can be detected by their reaction with monochloroamines.[2,3,38,248,249]

Phenols are more commonly separated before derivatisation by reversed-phase column liquid chromatography on chemically bonded stationary phases: μ-Bondapak C_{18}, Ultraspher C_{18}, Sorbax ODS, etc., with aqueous solutions of acetonitrile or methanol (often containing buffer systems, acetic acid, or counter-ions) as the eluent.[250-258] The phenols can also be separated by normal-phase chromatography on μ-Bondapak NH_2 or CN, μ-Porasil, Lichrosorb Si 60, Zipax CN, Sorbax Sil, and Sephasorb HP; the mobile phase is a mixture of organic solvents, including hexane, heptane, chloroform, isopropanol, etc.[18,23,252,257,258] The chromatographic separation is improved by impregnating the stationary phase with solutions of Fe(III) or of 8-hydroxyquinoline.[260] The phenols are identified by mass spectrometry, u.v. and i.r. spectrophotometry, or spectrofluorimetry.[9,13,20,239,252,256-258]

As in the case of acids, both schemes of chromato-spectrometric analysis can be used successfully for the determination of phenols.

11. The  and Groups

Quinones can be detected by oxidation, using their reaction with 2,4-dinitrophenylhydrazine, aromatic amines, polybasic phenols, and cyanoacetic ester,[1,3,10,38] but these methods are seldom compatible with separation, possibly because of the ease of reduction to the corresponding phenols.

The reaction of benzo- and naphthaquinones with benzoylsulphinic acid produces coloured and fluorescent dihydroxydiphenyl- or dihydroxyphenylnaphthylsulphones, which can be separated by TLC on silica gel or Siluphol.[247,261]

Silica gel, silica gel impregnated with $AgNO_3$, polyamide, or other sorbents can be used to separate quinones before derivatisation.[26,262] Analysis by column liquid chromatography (usually in the reversed-phase mode) is carried out on Porasil C_{18} or on Permophase ODS, with aqueous-organic eluents and u.v. detection.[9,18,239,263]

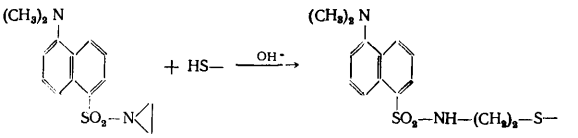
12. The −SH and −S−S− Groups

So far only a few derivatives compatible with the chromato-spectrometric determination of −SH compounds (or of compounds in which the −S−S− group has been reduced to −SH) have been reported.

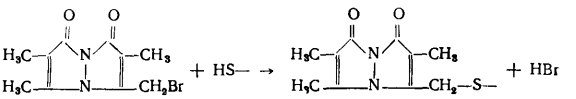
The interaction of thiols with S,S'-dithio-bis-(2-nitro)-benzoic acid at pH 8 produces coloured disulphides which can be separated, for example, by reversed-phase column liquid chromatography on Lichrosorb RP-18 with a methanolic phosphate buffer (pH 8.0); identification is by u.v. detection.[9,264]

2,4-Dinitrothioethers (produced by the reaction of thiols with 2,4-dinitrochlorobenzene) are easily separated by high-performance liquid chromatography on Lichrosorb RP-18 with an aqueous solution of acetonitrile. ¶

Thiols react with dansyl aziridene to give stable derivatives which are easily separated chromatographically:[8,265]



Monobromobimane reacts with thiols as follows:



The resulting compounds are fluorescent, and easily separable by chromatographic or electrophoretic methods.[266-268]

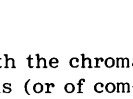
Fluorescent derivatives suitable for the analysis of thiols are obtained also from the reaction with 9-acridyl-, *N*-(*p*-2-benzimidazyl)phenyl-, and *N*-(7-dimethylamino-4-methylcoumarinyl)maleimides.[138,269,270] A new reagent for the preparation of fluorescent derivatives has recently been proposed: ammonium 7-fluorobenzo-2-oxa-1,3-diazole-4-sulphonate, which reacts with the −SH group at ~60 °C and pH ~9.5. Like NBD chloride, to which it is structurally similar, this preparation is relatively stable and is itself non-fluorescent. The analytical conditions for the column liquid chromatography of these compounds are discussed in Ref. 271.

Many papers describe the separation of thiols and disulphides by TLC before derivatisation. Silica gel or mixtures of silica gel with palladium chloride, aluminium oxide, or cellulose are used as sorbents.[26,80,272-274]

Visualisation of the −SH and −S−S− groups on the plates or in the eluates is possible both with universal and with more specific reagents: the complex of dithiofluorescein with *o*-hydroxymercurybenzoic acid, mixtures of sodium azide and iodine, mixtures of 3,5-di-t-butyl-1,2-benzoquinone and ferric chloride, and mixtures of 6,6'-dihydroxy-2,2'-dinaphthyl disulphide, the Dragendorf reagent, hydrogen sulphide solutions, and potassium hydroxide in aqueous butanol.[26,274-277]

Substances containing the −SH and −S−S− groups can be separated by column liquid chromatography (especially the reversed-phase variant) on μ-Bondapak C_{18}, Spherisorb ODS, HC Pellosil ODS, and other sorbents, with aqueous-alcoholic solutions at controlled pH.[10,138,278,279] The electrochemical detector[10,278-280] is found to be useful in the identification of these compounds.

Reagents for detecting thiols (after separation) by the colour or the fluorescence of the resulting compounds are proposed also in Refs. 281–284. Thus a mixture of *o*-phthalic aldehyde and taurine or other primary amine is shown to produce fluorescent isoindoles.

13. The  Groups

Compounds containing these groups are analysed mainly by TLC methods, with separation before derivatisation, using both pure and impregnated silica gel or aluminium oxide and

¶ see H.Langenhove, J.Chromatogr., 1983, **257**, 170.

various solvent systems.[26,80,272,273,285] Iodine, tetracyanoethylene, 2,3-dichloro-5,6-dicyano-1,3-benzoquinone, and other reagents are used for visualisation on the TLC plate.[26,80,273] If necessary, the analytical results are confirmed mass spectrometrically.[272,273,286]

14. The $-O-P(=O)(-O)-O$ Group

Separation of alkyl and aryl phosphates before derivatisation is carried out by TLC on silica gel or cellulose with various eluents, including benzene, methanol, and chloroform, and visualisation is by hydrolysis to the PO_4^{3-} anion followed by reaction (for example) with ammonium molybdate or vanadate to give coloured compounds.[26,287,290]

The separation before derivatisation of compounds containing these groups by normal- and reversed-phase column liquid chromatography with u.v. detection has been reported.[10,291,292]

15. The $-C-P<$ and $-C-P(=O)<$ Groups

Only a few reports of the chromato-spectrometric identification of groups containing the C–P bond have been published. Direct separation of a series of phosphonic acids has been achieved by TLC, with visualisation by oxidation to the PO_4^{3-} anion and reaction with ammonium molybdate or other similar reagent. Column chromatography has also been used, with various detectors.[26,289,293,294]

Some results on the determination of these groups are quoted in discussions of analytical methods for organophosphorus insecticides and their degradation products.[10,18,138,295,296]

IV. CONCLUSIONS

The results examined in this review show that a large volume of experimental information on the functional microanalysis of organic compounds by a combination of chemical reactions, chromatographic separation, and spectrometric identification is now available. Chromato-spectrometric methods are of interest for the determination of very small amounts (10^{-9}–10^{-11} g) of organic substances of various types, and their potential performance in this respect is far superior to that of classical methods of functional analysis.

Relative assessments of the reagents used in chromato-spectrometric methods have not so far been compiled: this hinders the choice of the best reagent for the analysis of complex mixtures. We have therefore combined published data and experimental results obtained in our laboratory to produce a list of some of the characteristics of the most commonly used reagents, which are often known to be the optimum choice for specific chromato-spectrometric analyses (see Table). This tabulation should prove useful in the selection of reagents for the analysis of various types of material.

Reactive chromato-spectrometric methods have found practical applications in the micro-analysis of many organic substances for functional groups, but the scope of their exploitation is still far from reaching its full potential. An effort is needed to extend the area of practical application of chromato-spectrometric methods, preferably by simplifying the various stages and the automation procedures of the analysis.

Characteristics of some reagents used in chromato-spectrometric methods.

Reagent	Application: before separation	Application: after separation	Groups	Method of detection
3,5-Dinitro- or 4-nitrobenzoyl chloride	+	–	$-NH_2$; >NH, >C–OH; $-C_6H_4-OH$	Col., u.v., MS
Dansyl chloride	+	–	$-NH_2$; >NH; $-C_6H_4-OH$	U.v., fl., MS
2,4-Dinitrofluorobenzene	+	–	$-NH_2$; >NH; –SH; >C–OH; $-C_6H_4-OH$	Col., u.v., MS
NBD chloride	+	+	$-NH_2$; >NH	Col., u.v., fl MS
Phenyliso- or phenylisothiocyanate	+	–	$-NH_2$; >NH; $-C_6H_4-OH$; >C–OH	U.v., MS
o-Phthalic aldehyde	+	+	$-NH_2$	U.v., fl.
4-Phenyl-*spiro*(furan-2), 3H-1′-phthalan-3,3′-dione (fluram)	+	+	$-NH_2$	Fl., u.v.
Ninhydrin	–	+	$-NH_2$	Col., u.v.
Diazotised sulphanilic acid or 4-nitroaniline	+	+	$-C_6H_4-NH_2$; $-C_6H_4-OH$	Col., u.v.
Dragendorf reagent	–	+	>N; $>\overset{+}{N}-$	Col.
N-4-Nitrobenzyl-*N*-propylamine	+	–	$-N=C=O$	U.v.
Acetone and NaOH	–	+	$-C_6H_3(NO_2)_2$ and $-C_6H_2(NO_2)_3$	Col., u.v.
2,4-Dinitro- or 4-nitrophenylhydrazine	+	–	>C=O	Col., u.v., MS
Dansylhydrazine	+	–	>C=O	Fl., u.v., MS
4-Nitrobenzyloxyamine	+	–	>C=O	U.v., MS
N′-Methylnicotinamide chloride	+	+	$-CH_2-C(=O)<$	Fl.
Dimedon	+	–	$H-C(=O)<$	Col., fl.
N,*N*′-Dimethylamino-4-aniline	+	–	$H-C(=O)<$	Col.
4-Bromo- or 4-nitrophenacyl bromide	+	–	–COOH	U.v., MS
2-Naphthacyl bromide	+	–	–COOH	Fl., u.v., MS
p-Nitrobenzyl-*N*,*N*′-diisopropylisourea	+	–	–COOH	Col., u.v.
4-Bromomethyl-7-methoxycoumarin	+	–	–COOH	Fl., u.v.
1-Naphthyl- or 9-anthryldiazomethane	+	–	–COOH	Fl., u.v.
o-Phenylenedimaine	+	–	$-C(=O)-C(=O)-$	Fl., u.v.
Ce^{4+} salts	–	+	–COOH; >C–OH; $-C_6H_4-OH$	Fl.
Na vanadate and 8-hydroxyquinoline	–	+	>C–OH	Col.
4-Aminoantipyrine	+	+	$-C_6H_4-OH$	Col.
5,5′-Dithio-*bis*(2-nitro)benzoic acid	–	+	–SH	Col.
Tetracyanoethylene	–	+	=S; =S=O; $>S(=O)_2$; >N	Col., MS
Ammonium molybdate	–	+	$-O-P(=O)(-O)-O$	Col.

Symbols denoting the methods: U.v., by absorption in the u.v. region of the spectrum; Fl., by fluorescence; MS, by mass spectrometry; Col., by visual colour.

Further work on the development of a rational system of functional micro-analysis of organic compounds by chromatospectrometric methods is needed. Substantial improvements in the sensitivity of the determination (in particular, by fluorimetric and mass spectrometric methods) should result from the use of analytical lasers.

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Catalysis by Metalloporphyrins of Reactions Involving Oxidation by Molecular Oxygen and Oxygen-containing Compounds

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Data on the catalysis by metalloporphyrins of reactions involving the oxidation of organic compounds by molecular oxygen, iodosobenzene, sodium hypochlorite, hydroperoxides, and peracids are surveyed and analysed. The possible mechanisms of the catalytic action of metalloporphyrins in these systems are proposed. The promising trends in the research designed to create, on the basis of metalloporphyrins, new catalytic systems for the selective oxidation of organic compounds under mild conditions are outlined.
The bibliography includes 188 references.

CONTENTS

I.	Introduction	215
II.	Reactions involving molecular oxygen	216
III.	Oxidation by iodoso-compounds	219
IV.	Reactions of organic compounds with sodium hypochlorite	222
V.	The interaction of olefins with hydroperoxides and peracids	222

I. INTRODUCTION

Metalloporphyrin compounds[1-26] constitute the prosthetic groups in many enzymes—oxygenases, peroxidases, and others.[27-34] In particular, haemin forms part of the composition of cytochromes P-450, which are responsible for the detoxication of living organisms and which effect the hydroxylation of saturated and aromatic hydrocarbons and the epoxidation of olefins by molecular oxygen in their cells. The unique structure of metalloporphyrins, which contain the planar porphyrin ring with an extensive π-conjugation system and a central variable-valence metal ion,[7,8,35,36] determines their high catalytic activity. Oxygen-containing compounds such as hydroperoxides[37-43] and iodosobenzene[44-47] can successfully replace oxygen as the corresponding electron donor [acceptor] in selective oxidation reactions catalysed by cytochromes P-450.

The problem of modelling the catalytic functions of cytochromes P-450 by synthetic metalloporphyrins is of crucial importance at the present time. Its solution will make it possible to create new catalytic systems for the selective oxidation of organic compounds by molecular oxygen under mild conditions. The development of highly selective industrial methods of synthesis of epoxides and alcohols is an important task in present day chemistry.

One of the central aspects of the relevant research involves the study of the mechanisms of the catalytic action of metalloporphyrins in reactions involving the oxidation of organic substrates by molecular oxygen and oxygen-containing compounds. The understanding of these mechanisms will assist

in the further development of studies designed to create new effective catalytic systems, based on metalloporphyrins, for selective oxidation. Furthermore, investigation of the mechanisms of the catalytic action of synthetic metalloporphyrins should help in understanding the mechanisms of the action of porphyrin-containing enzymes which have not so far been elucidated. This is very important not only for the development of biochemistry but also for chemotherapy.

The possible mechanisms of the catalytic action of metalloporphyrins in the oxidation of organic compounds by molecular oxygen, iodosobenzene, sodium hypochlorite, hydroperoxides, and peracids are proposed in this review on the basis of current ideas and the analysis of experimental data for such systems.

II. REACTIONS INVOLVING MOLECULAR OXYGEN

The results of studies of the catalysis by metalloporphyrin complexes of reactions involving oxidation by molecular oxygen have already been surveyed.[25] Here we shall not consider these data again and the bibliography of the previous review will be merely supplemented by a number of publications[24,48-89] and the possible mechanisms of these reactions will be discussed.

As a rule, metalloporphyrins initiate the radical chain autoxidation of organic substrates (alkanes, olefins, and aldehydes) via the following mechanism. Molecular oxygen is coordinated to the metal ion of the metalloporphyrin (P–M), forming a charge-transfer complex whose electronic structure depends on the nature of the metal. This can be both a superoxide complex, for example (Py)TPhP-$Co^{3+}...O_2^-$ [90-98] (where Py = pyridine and TPhP = tetraphenylporphin ligand) and a peroxide complex, whose formation has been suggested for TPhP-$Mn^{4+}...O_2^{2-}$.[98-101] These complexes initiate the chain in the autoxidation of organic substrates, abstracting the mobile hydrogen from the latter:

$$P\text{-}M^+ \ldots O_2^- + RH \rightarrow P\text{-}M^+ \ldots O_2H^- + R^\cdot ,$$

where RH is the oxidisable substrate. In the case of olefins, the initiation of the autoxidation is also possible as a result of the addition of the superoxide (or peroxide) complex to the double bond:

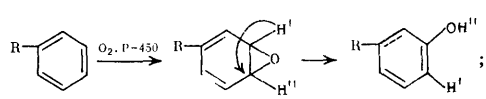
$$P\text{-}M^+ \ldots O_2^- + \rangle C{=}C\langle \rightarrow -\overset{|}{C}-\overset{|}{C}\cdot- \quad (-O-O-M^+\text{-}P)$$

Fe(III)-protoporphyrin (IX) (haemin) is known to occur as the prosthetic group in the composition of mono-oxygenating enzymes–cytochromes P-450 (the complexes of their reduced forms with carbon monoxide have a characteristic Soret absorption band at 450 nm). The nature of the axial ligand linked to haemin cannot be regarded as firmly established. It has been suggested that the iron ion in cytochrome P-450 is linked to cysteine and histidine residues.[27]

Cytochromes P-450 catalyse the following reactions involving oxidation by molecular oxygen:[102]

(1) hydroxylation of aliphatic hydrocarbons;

(2) hydroxylation of aromatic hydrocarbons with formation of an intermediate epoxidation product and the migration of hydrogen atoms:[103,104]



; (1)

(3) epoxidation of olefins;

(4) mono-oxygenation of sulphur- and nitrogen-containing organic compounds.

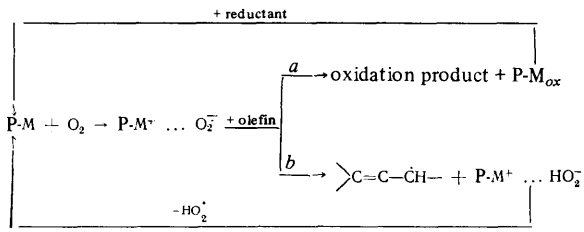
It is noteworthy that both in the cells of living organisms and under laboratory conditions cytochromes P-450 act as mono-oxygenating enzymes only in the presence of a reductant, which is necessary to reduce the second atom of the oxygen molecule to water. The overall equation of the mono-oxygenation reaction is:[102]

$$S + O_2 + DH_2 \rightarrow SO + D + H_2O ,$$

where S is the substrate and DH_2 the reducing agent. The respiratory chain of mitochondria, NADH (nicotinamide-adenine dinucleotide) or NADPH (nicotinamide-adenine dinucleotide phosphate), reduced flavins, and tetrahydropteridines can play the role of reductants.

It is striking that the modelling of the mono-oxygenating activity of cytochromes P-450 by metalloporphyrin complexes has been achieved only in the presence of a suitable electron donor. The results of these studies are presented in Table 1. Only in the presence of a reductant in the system does the metalloporphyrin act as an agent transferring one of the atoms of molecular oxygen to the oxidisable substrate. In the absence of a reductant, the free-radical chain autoxidation is initiated with formation of a set of products characteristic of this process.[110]

The mechanism of the processes occurring in model systems consisting of a metalloporphyrin, oxygen, and an oxidisable substrate can be represented as follows. A superoxide (or peroxide) complex, which is capable of initiating the free-radical chain oxidation by abstracting a mobile hydrogen atom from the substrate molecule (or by adding to the double bond of the olefin) (pathway *b* in the scheme below), is formed initially. In addition, the complex functions as an agent transferring oxygen to the oxidisable compound (pathway *a*), although this process cannot be regarded as truly catalytic because the metalloporphyrin is then converted into the oxidised form and is immediately eliminated from the system. The added reductant regenerates the active form of the metalloporphyrin and completes the catalytic cycle of the model oxygenation reaction. However, under these conditions there is a possibility of the formation of secondary products via the interaction of the oxidation product with the reductant.



The model mono-oxygenating systems are much less active than the natural enzymes. Thus in the presence of TPhP-MnCl the yields of the olefin oxidation products range from 3 to 32% after 24 h and between 1.7 and 32 catalytic cycles are accomplished during this period (Table 1). TPP-MnCl is most active in the oxidation of steroids, where 170–230 catalytic cycles take place in 1–3 h and the yield of the product reaches 78–82%.[48,49] The activity of haemin in the oxidation of cyclohexane in an aqueous acetone medium is less than that of the natural hydroxylating system by a factor of 50,[108] while in the hydroxylation of aniline in a highly alkaline medium it is less by a factor of 4.[109] The higher effectiveness of natural cytochromes P-450 compared with the model systems is apparently associated with the fact that the protein component of the enzyme ensures the optimum spatial orientation of the substrate with respect to the oxygen complex of

haem and at the same time creates the optimum micro-environment for the active centre (for example, the necessary basicity).[109]

Table 1 shows that the character of the products and the selectivity of the oxidation reactions in the presence of the model catalytic system depend significantly on the nature of the reductant. A mild reducing agent, such as sodium ascorbate, makes it possible to achieve the epoxidation of olefins (cyclohexene, hex-1-ene, 2,3-dimethylbut-2-ene, and styrene) with 100% selectivity,[77] while in the presence of powerful reducing agents, namely sodium and tetra-n-butylammonium tetrahydroborates, the reaction usually results in the formation of a mixture of saturated alcohols and ketones[48, 49, 106] (only Δ^5-steroids give rise to single products—5-α-hydroxysteroids).

Cyclohexene differs from other unsaturated hydrocarbons by the presence of allyl oxidation products—cyclohex-2-en-1-ol,[84, 105, 106] and cyclohex-2-en-1-one.[107] The influence of the nature of the reductant on the composition of the reaction products has also been traced in relation to cyclohexene: a

Table 1. Oxidation of organic compounds by oxygen at room temperature in the presence of TPhP-MnCl and a reductant.

No.	Substrate	Reductant	Solvent	τ, h	Products	Yield, %		Refs.
						α_o	α_c	
1	Cyclohexene	$NaBH_4$	Benzene–ethanol	—	Cyclohexanol	2.0	1 224	[105]
					Cyclohex-2-en-1-ol	0.5	306	
2	Cyclohexene*	$NaBH_4$	THF	48—130	Cyclohexanol	10	20 000	[84]
					Cyclohex-2-en-1-ol	0.2	400	
3	Cyclohexene	$(NBu_4)BH_4$	CH_2Cl_2	24	Cyclohexanol	16	1 600	[106]
					Cyclohex-2-en-1-ol	8	800	
4	Cyclohexene**	H_2-colloidal Pt	Ethanol	63	Epoxycyclohexane	19	6 470	[107]
					Cyclohex-2-en-1-one	13	440	
5	Cyclohexene***	Na ascorbate	Benzene–water (pH 8.5)	10	Epoxycyclohexane	—	230	[77]
6	Cyclo-octene	$(NBu_4)BH_4$	CH_2Cl_2	24	Cyclo-octanone	20	2 000	[106]
					Cyclo-octanol	8	800	
7	Oct-1-ene	$(NBu_4)BH_4$	CH_2Cl_2	24	2-Octanone	7	700	[106]
					2-Octanol	9	900	
8	Styrene	$(NBu_4)BH_4$	CH_2Cl_2	24	Acetophenone	7	700	[106]
					1-Phenylethanol	17	1 700	
9	Styrene***	Na ascorbate	Benzene–water (pH 8.5)	10	Styrene oxide	—	600	[77]
					2-Phenylethanal	—	80	
10	1-Phenylpropene	$(NBu_4)BH_4$	CH_2Cl_2	24	Propiophenone	12	1 200	[106]
					1-Phenyl-1-propanol	20	2 000	
11	Ethylene	$NaBH_4$	DMF	24	Ethanol	3	167	[48, 49]
12	Propene	$NaBH_4$	DMF	24	2-Propanone	4	222	[48, 49]
					2-Propanol	6	333	
13	Hex-1-ene	$NaBH_4$	DMF	24	2-Hexanone	9.8	975	[48, 49]
					2-Hexanol	3.2	325	
14	Hex-1-ene	$NaBH_4$	Benzene–ethanol	24	2-Hexanone	2.0	110	[48, 49]
					2-Hexanol	7.6	420	
					1,2-Epoxyhexane	0.5	28	
15	Hex-2-ene	$NaBH_4$	DMF	24	2-Hexanone	6.0	600	[48, 49]
					3-Hexanone	6.0	600	
					2-Hexanol	1.5	150	
					3-Hexanol	1.5	150	
16	Hex-2-ene	$NaBH_4$	Benzene–ethanol	24	2-Hexanone	0.5	26.6	[48, 49]
					3-Hexanone	0.5	26.6	
					2-Hexanol	5.2	287	
					3-Hexanol	5.2	287	
					2,3-Epoxyhexane	0.7	40	
17	Hex-1-ene***	Na ascorbate	Benzene–water (pH 8.5)	10	1,2-Epoxyhexane	—	30	[77]
18	2,3-Dimethylbut-2-ene***	Na ascorbate	Benzene–water (pH 8.5)	10	2,3-Epoxy-2,3-dimethylbutane	—	340	[77]
19	D-Androst-5-en-3β-ol	$NaBH_4$	Benzene–ethanol	2	D-Androstane-3β,5α-diol	78	22 000	[48, 49]
20	D-Cholest-5-en-3β-ol	$NaBH_4$	DMF	2	D-Cholestane-3β,5α-diol	80	17 900	[48, 49]
21	D-Cholest-5-en-3β-ol	$NaBH_4$	Benzene–ethanol	2	D-Cholestane-3β,5α-diol	82	23 000	[48, 49]
22	Cyclohexane***	Na ascorbate	Benzene–water (pH 8.5)	10	Cyclohexanol	—	40	[77]
					Cyclohexanone	—	300	
23	Cyclohexane****	*o*-HS—C_3H_4—CO_2H	Water–acetone	0.4	Cyclohexanol	0.8	200	[108]
					Cyclohexanone	0.4	100	
24	Heptane***	Na ascorbate	Benzene–water (pH 8.5)	10	4-Heptanone	—	300	[77]
					3-Heptanone	—	130	
					2-Heptanone	—	70	
25	Adamantane	H_2-colloidal Pt	Ethanol	14	1-Adamantanol	1.8	314	[107]
					2-Adamantanol	0.2	36	
					2-Adamantanone	0.12	21	
26	Toluene***	Na ascorbate	Benzene–water (pH 8.5)	10	Benzaldehyde	—	400	[77]
27	Aniline****	NADH (or NADPH)	Water (pH > 11)		*p*-Aminophenol	1.5	300	[109]
28	Cyclohexanol***	Na ascorbate	Benzene–water (pH 8.5)	10	Cyclohexanone	—	1 500	[77]
29	4-Heptanol***	Na ascorbate	Benzene–water (pH 8.5)	10	4-Heptanone	—	1 300	[77]
30	Benzyl alcohol***	Na ascorbate	Benzene–water (pH 8.5)	10	Benzaldehyde	—	8 700	[77]

Notation: τ is the reaction time and α_o and α_c are the yields of the product recalculated in terms of the compound oxidised and the catalyst respectively.

*The catalyst was OEP-RhCl, where OEP = octaethylporphyrin ligand.
**1-Methylimidazole was added to the system.
***Two-phase system containing a phase transfer agent (methyltrioctylammonium chloride).
****The catalyst was haemin.

mixture of cyclohexanol and allyl alcohol is obtained in the presence of $NaBH_4$,[105] when gaseous hydrogen and colloidal platinum are used, the products are epoxycyclohexane and an αβ-unsaturated ketone,[107] while epoxycyclohexane is formed on treatment with sodium ascorbate.[77] Saturated hydrocarbons are oxidised in the presence of the model catalytic systems with formation of alcohols and ketones.[77,107,108]

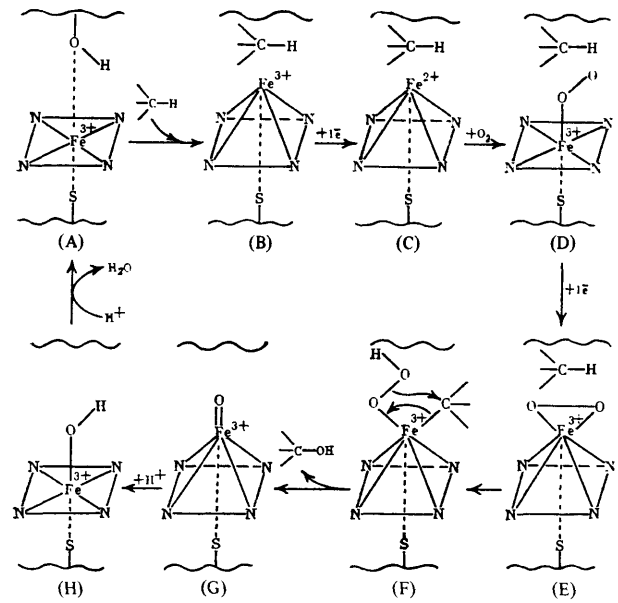
A characteristic feature of the oxidation of olefins on treatment with the model systems is an increase in the rate of reaction with increasing nucleophilicity of the double bond. Thus the rate of oxidation in the O_2–TPhP–MnCl–$NaBH_4$ system increases in the sequence ethylene < propene < hex-1-ene < hex-2-ene;[48,49] in the O_2-TPhP–MnCl–sodium ascorbate two-phase system containing a phase-transfer agent, the reactivity of olefins increases in the following sequence: hex-1-ene < cyclohexene < 2,3-dimethylbut-2-ene < styrene;[77] in the O_2–TPhP-MnCl–$(NBu_4)BH_4$ system 1-phenylpropene is more reactive than styrene;[106] in the O_2–TPhP-MnCl–H_2–colloidal platinum system, *cis*-oct-2-ene is oxidised approximately 18 times faster than hex-1-ene.[107] The very high reactivity of trisubstituted steroid olefins in oxidation by the O_2–TPhP-MnCl–$NaBH_4$ system cannot apparently be explained solely by the nucleophilic properties of the double bond. We shall return to this problem later. The analogous influence of electron-donating substituents on the rate of mono-oxygenation has been noted also for enzyme systems.[111]

Another feature of the oxidation of olefins in the presence of the model catalytic systems is the regioselectivity of the process. The oxidation involves the most substituted carbon atom: only secondary alcohols and ketones are formed from asymmetrically substituted olefins (oct-1-ene, styrene, 1-phenylpropene,[106] propene, and hex-1-ene[48,49]).

The third feature is the significant role of steric factors, which is indicated by the activity of *cis*-oct-2-ene being greater by an order of magnitude than that of its *trans*-isomer in the oxidation reaction catalysed by the O_2–TPhP-MnCl–H_2–colloidal platinum system.[107]

The mechanism of the action of hydroxylating enzyme systems based on cytochromes P-450 has not so far been established. The nature of the oxidising agent has not been determined by direct procedures in any of the systems. Several mechanisms have been discussed in the literature.[41,102,112–118] One of these, presented below (Scheme 1),[102] reflects in our view the electrophilic nature of the reaction most convincingly. The catalytic cycle begins with the conversion of the hexacoordinate Fe^{3+} complex in a low-spin state (A) into a pentacoordinate Fe^{3+} complex in a high-spin state (B) as a result of the binding of the hydrocarbon to be oxidised by the protein component of the enzyme. The one-electron reduction of compound (B) leads to a pentacoordinate Fe^{2+} complex in a high-spin state (C) capable of binding oxygen with formation of a low-spin Fe^{3+} superoxide complex (D). The states (A), (B), (C), and (D) have been thoroughly characterised,[115,119] but the mechanism of the transfer of oxygen from the complex (D) to the substrate being oxidised has not been finally elucidated.

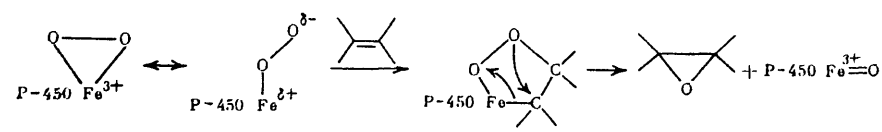
Scheme 1



The addition of a second electron to (D) can lead to the formation of the Fe^{3+} peroxide complex (E). The mechanism of this addition has also not been established hitherto. Presumably the porphyrin ligand gives up an electron, being converted simultaneously into a porphyrin radical-cation. The heterolytic cleavage of the C–H bond is accompanied by the simultaneous opening of the Fe^{3+}–peroxo bond and leads to a very unstable alkyl Fe^{3+} hydroperoxide (F), which decomposes with formation of the oxidation product – an alcohol and the Fe^{3+} oxo-complex (G). The latter hydrolyses to the Fe^{3+} hydroxo-complex (H), the initial complex (A), and water.

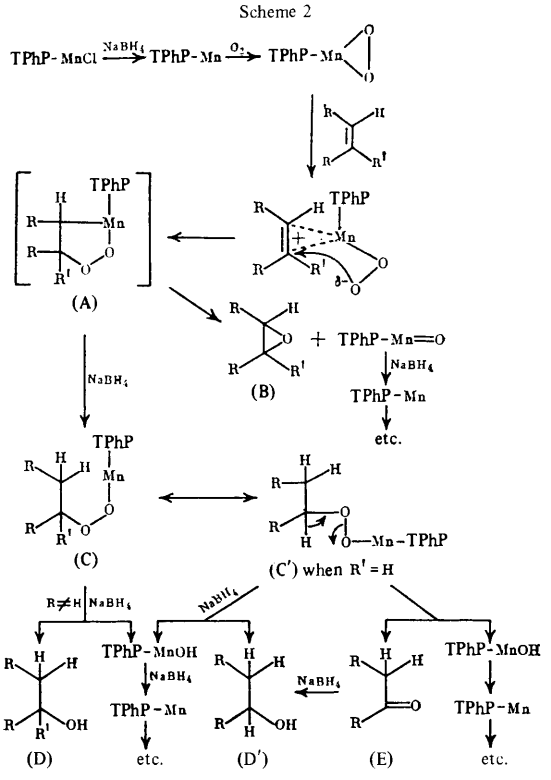
This mechanism agrees with the large isotope effect (k_H/k_D = 11.5) in the norbornane hydroxylation reaction in the presence of cytochromes P-450,[120] which presupposes the activation and cleavage of the C–H bond. This scheme also agrees with the formation of the Fe^{3+} oxo-complex, detected in the two-electron oxidation of chloroperoxidase.[121] The intermediate formation of the same complex has been postulated in the hydroxylation of hydrocarbons by hydrogen peroxide in the presence of iron ions.[122]

The mechanism of the epoxidation of olefins and aromatic compounds in the presence of cytochromes P-450 presupposes[102] the insertion of an olefin molecule in the 1,3-dipolar metal–peroxo bond of the complex (E) (Scheme 1) with formation of an intermediate five-membered ring, which decomposes into an epoxy-compound and an oxo-complex. Aromatic epoxides then rearrange to phenols.



A mechanism of the oxidation of olefins in the presence of the O_2–TPhP-MnCl–reductant model system has been proposed,[49] which takes into account all the characteristic features of this process, namely the influence of the nature of the reductant on the composition of the reaction products, the formation of a single product (a tertiary alcohol from trisubstituted olefins and a ketone and a secondary alcohol from mono- and di-substituted olefins) when powerful reductants are used, and the regioselectivity of the oxidation and the dependence of the rate of the latter on the nucleophilicity of the double bond and steric factors (Scheme 2).

Scheme 2



In the first stage of the process the reductant (in the given instance $NaBH_4$) converts TPhP-Mn^{3+}Cl into TPhP-Mn^{2+}, which interacts with molecular oxygen to form an oxygen complex having the peroxide structure: TPhP-Mn^{4+}...O_2^{2-};[98-101] according to Hansen and Hoffman,[100] the Mn^{4+} ion in this complex lies 0.5 Å above the plane of the porphyrin ligand. The nucleophilic olefin is coordinated to the most electrophilic component of this complex – the Mn^{4+} ion, after which the olefin molecule is inserted in the dipolar Mn-peroxo bond with formation of the cyclic intermediate (A). The regioselectivity of the reaction is determined by the laws governing electrophilic addition. The epoxide (B) can be formed as a result of the disproportionation of the intermediate (A). When weak reductants are used, the epoxide is the only product of the reaction. However, in model systems containing a powerful reductant, the reductive cleavage of the Mn–C bond in the cyclic intermediate (A) apparently takes place with formation of a peroxide complex (C or C'). The subsequent reactions of this complex should depend on the degree of substitution of the carbon atom linked to the peroxy-group. The reduction of the O–O bond in the complex (C) with a tertiary carbon atom by sodium tetrahydroborate leads to the tertiary alcohol (D) and TPhP-MnOH, which enters into a new catalytic cycle. The peroxide complex for the secondary carbon atom (C') is capable, on the one hand, of being reduced by $NaBH_4$ to the secondary alcohol (D') and TPhP-MnOH and, on the other hand, it can disproportionate to the ketone (E) and TPhP-MnOH. An alternative pathway to the formation of secondary alcohols involves the reduction of the ketone (E) by sodium tetrahydroborate.

The order in which the Mn–C and O–O bonds are ruptured in the cyclic intermediate (A) is unimportant, since in both cases the ketone (E) and the alcohols (D) and (D') are formed as primary products without manganese.

Although this mechanism is so far only tentative, it must be emphasised that all its stages have reasonable analogies. Thus reactions involving the disproportionation of secondary peroxides to the carbonyl compounds (C') → (E) and the reduction of M–C bonds by tetrahydroborate (A) → (C) are known.[123,124]

Analysis of the products of the oxidation of olefins in the presence of model catalytic systems (Table 1) permits the conclusion that model systems containing milder reductants, for example, sodium ascorbate, are closer in their action to natural cytochromes P-450: the intermediate (A) disproportionates in their presence with formation of epoxy-compounds via the reaction (A) → (B).

The oxidation of tertiary olefins, in particular of the steroids D-androst-5-en-3β-ol and D-cholest-5-en-3β-ol, by the O_2-TPhP-MnCl–$NaBH_4$ system leads to a single product (corresponding to a tertiary alcohol) via the reaction (C) → (D), since the formation of a ketone is in this instance impossible. The high reactivity of steroids in this reaction is apparently associated not only with the enhanced nucleophilicity of the double bond owing to the presence of substituents but also with the reduced energy of the C=C bond owing to the strain in the molecular structure of the steroids. This facilitates the formation of the cyclic intermediate complex (A), i.e. diminishes the activation barrier to the reaction.

Presumably the oxidation of saturated hydrocarbons in the presence of metallo-porphyrin catalytic systems proceeds via the intermediate formation of a hydroperoxy-compound, which then decomposes and is converted into an alcohol or ketone. It may be that this mechanism is also responsible for the formation of the products of the allyl oxidation of cyclohexene by the O_2–TPhP-MnCl–$NaBH_4$ system.

In conclusion of this Section, it must be emphasised that the above mechanisms make it possible to regard the selective oxidation of hydrocarbons by molecular oxygen in the presence of cytochromes P-450 and synthetic metalloporphyrins as a special case of reactions which are accelerated in the presence of transition metal complexes and involves the insertion of a molecule of the coordinated substrate in the metal–nucleophile bond (polymerisation, hydrogenation, hydroformylation and other processes belong to reactions of of this kind).[125]

III. OXIDATION BY IODOSO-COMPOUNDS

Metalloporphyrins catalyse the oxidation of hydrocarbons by iodosobenzene[126-134] without the involvement of reductants (Table 2). The results presented show that the catalytic effects of the Mn-porphyrins, on the one hand, and Fe- and Cr-porphyrins, on the other, are different. The difference is manifested in the first place in the composition of the reaction product. Fe- and Cr-porphyrins usually catalyse the selective epoxidation of olefins and the hydroxylation of saturated and aromatic hydrocarbons. Cyclohexene is an exception, being oxidised in the presence of Fe-porphyrins predominantly to an epoxide (75–95%) with formation of a small amount of cyclohex-2-en-1-ol (5–25%);[126,127] mainly

Table 2. Oxidation of hydrocarbons by iodosobenzene in the presence of metalloporphyrins at 25 °C in solution in CH_2Cl_2.

Substrate	Catalyst	Products	W, %	α, %*	Refs.
Cyclohexene	TPhP-FeCl	Epoxycyclohexane	78	70 (430)**	[126]
		Cyclohex-2-en-1-ol	22		
Cyclohexene	TPhP-FeCl	Epoxycyclohexane	75	65 (650)	[127]
		Cyclohex-2-en-1-ol	25		
Cyclohexene	TFPhP-FeCl	Epoxycyclohexane	95	100 (1000)	[126]
		Cyclohex-2-en-1-ol	5		
Cyclohexene	TPhP-CrCl	Epoxycyclohexane	4	66	[128]
		Cyclohex-2-en-1-ol	75		
		Cyclohex-2-en-1-one	21		
Cyclo-octene	TPhP-CrCl	Epoxycyclo-octane	100	28	[128]
Norbornene	TPhP-CrCl	Norbornene oxide	100	90	[128]
Sytrene	TPhP-CrCl	Styrene oxide	100	65	[128]
cis-Stilbene	TPhP-FeCl	*cis*-Stilbene oxide	100	82	[126, 129]
cis-Stilbene	TPhP-CrCl	*cis*-Stilbene oxide	100	23	[128, 129]
cis-Stilbene	TPhP-MnCl	*cis*-Stilbene oxide	49	88	[130]
		trans-Stilbene oxide	61		
cis-Stilbene	T(*o*-CH_3O-Ph) P-MnCl	*cis*-Stilbene oxide	74		
		trans-Stilbene oxide	26	87	[130]
trans-Stilbene	TPhP-FeCl	*trans*-Stilbene oxide	100	traces	[126, 129]
trans-Stilbene	TPhP-CrCl	*trans*-Stilbene oxide	100	17	[128, 129]
trans-Stilbene	TPhP-MnCl	*trans*-Stilbene oxide	100	53	[130]
Cyclohexa-1,3-diene	TPhP-FeCl	1,2-Epoxycyclohex-3-ene	100	74	[126]
Cyclohexane	TPhP-FeCl	Cyclohexanol	100	8	[126]
Cyclohexane	TPhP-FeCl	Cyclohexanol	100	5 (50)	[127]
Cyclohexane	TFPhP-FeCl	Cyclohexanol	100	71 (710)	[127]
Cyclohexane	TPhP-MnCl	Cyclohexanol	71	70	[130]
		Cyclohexyl chloride	29		
Cyclohexane	TPhP-MnBr	Cyclohexanol	65		
		Cyclohexanone	8	40	[131]
		Cyclohexyl chloride	25		
		Bicyclohexyl	2		
Cyclohexane***	TPhP-FeCl	Cyclohexanol	91		
		Cyclohexanone	9	26.5 (530)	[133]
Cyclohexane***	TPhP-MnCl	Cyclohexanol	91		
		Cyclohexanone	9	33 (660)	[133]
Cyclohexane***	TPhP-CrCl	Cyclohexanol	50	8 (160)	[133]
		Cyclohexanone	50		
Cyclohexane***	TPhP-CoCl	Cyclohexanol	77		
		Cyclohexanone	23	6.5 (130)	[133]
n-Heptane***	TPhP-FeCl	2-Heptanol	33		
		3-Heptanol	38		
		4-Heptanol	19	20 (400)	[133]
		2-Heptanone	3		
		3-Heptanone	4		
		4-Heptanone	2		
Adamantane	TPhP-FeCl	1-Adamantanol	92	13	[126]
		2-Adamantanol	8		
Adamantane	TPhP-MnCl	1-Adamantanol	50		
		2-Adamantanol	18		
		1-Chloroadamantane	11	80	[130]
		2-Chloroadamantane	12		
Norcarane	TPhP-MnCl	2-Norcaranol	50		
		2-Hydroxymethylnorcarane	20		
		2-Chloromethylnorcarane	22	—	[130]
		2-Chlorononcarane	5		
		2-Norcaranone	1		
Anisole****	TPhP-FeCl	*o*-Methoxyphenol	10		
		p-Methoxyphenol	50	2	[127]
		Phenol	40		
Anisole****	TFPhP-FeCl	*o*-Methoxyphenol	26	11.4	[127]
Anisole****	TFPhP-FeCl	*p*-Methoxyphenol	70	11.4	[127]
		Phenol	4		
Anisole****	TPhP-MnCl	Phenol	74		
		p-Methoxyphenol	1	16.1	[127]
		Diphenyl ether of ethylene glycol	25		

Notation: TFPhP-FeCl = Fe-tetra(pentafluorophenyl)-porphin chloride; T(o-CH_3O-Ph)P-MnCl = Mn-tetra-(*o*-methoxyphenyl)porphin chloride; α = yield of products; *W* = proportion of product.

*Yield expressed as a percentage relative to iodosobenzene; the yield expressed in relation to the catalyst is given in brackets (our calculation based on the authors' data).

**The overall yield with respect to cyclohexene is 2.2%.

***Solution in benzene.

****Without a solvent.

cyclohex-2-en-1-ol (75%) is formed in the presence of TPhP-CrCl with a smaller amount of cyclohex-2-en-one (21%) and only 4% of epoxycyclohexane.[128] On the other hand, Mn-porphyrins catalyse the non-stereospecific epoxidation of stilbene[130] and the oxidation of saturated and aromatic hydrocarbons[127,130,131,133] with formation of a large set of products and, when the reaction is carried out in chlorinated solvents, chloro-products are also formed. Another difference between the effects of Mn-porphyrins, on the one hand, and Fe- and Cr-porphyrins, on the other, concerns the stereospecificity of the olefin epoxidation reaction. The epoxidation of *cis*-stilbene in the presence of TPhP-FeCl and TPhP-CrCl[126,128,129] results in the exclusive formation of *cis*-stilbene oxide: *trans*-stilbene is converted in the presence of TPhP-CrCl solely into the *trans*-oxide (the reaction does not occur in the presence of TPhP-FeCl). In this reaction the Mn-porphyrin catalysts[130] do not exhibit stereospecificity – a mixture of the *cis*- and *trans*-oxides is formed in the oxidation of *cis*-stilbene.

The above data permit the conclusion that the mechanisms of the catalytic action of Mn-porphyrins, on the one hand, and the Fe- and Cr-porphyrins, on the other, in the oxidation of hydrocarbons by iodosobenzene are different: Mn-porphyrins catalyse a radical process, while Fe- and Cr-porphyrins act as oxygen atom-transferring agents. The hydroxylating and epoxidising iodosobenzene–P-FeCl (or P-CrCl) system constitutes a functional model of cytochrome P-450. Additional evidence of this is provided by the following facts: the TPhP-FeCl–PhIO system is effective in the dealkylation reactions of *NN*-dimethylaniline[135] and anisole,[43,136] which are characteristic of cytochromes P-450;[43, 137,138] in the hydroxylation of anisole by iodosobenzene and TFPhP-FeCl, it has been established by the isotope tracer method that hydrogen atoms migrate[127] [see Eqn.(1)], which is characteristic of the hydroxylation of aromatic hydrocarbons in the presence of cytochromes P-450;[104] furthermore, iodosobenzene successfully substitutes molecular oxygen and the reductant in oxidation reactions catalysed by these enzymes.[44,47]

In the PhIO–P-MCl systems agents responsible for direct oxygen transfer to the substrate are oxo-complexes of metalloporphyrins containing the metal in a high oxidation state.[126,128-131,139-144] It has been shown that the reaction of P-MCl with PhIO results in the formation of iodobenzene (absorption bands at 1018 and 999 cm^{-1} appear in the infrared spectra)[128,129] and the oxo-complex of the metalloporphyrin (the absorption band at 1026 cm^{-1} corresponds to the vibrations of the Cr=O bond[128] and that at 1060 cm^{-1} to the vibrations of the Mn=O bond[145]). The addition of labelled water $H_2^{18}O$ to the PhIO–TPhP-CrCl system results in the disappearance of the 1026 cm^{-1} band from the infrared spectrum and the appearance of a band at 982 cm^{-1} corresponding to the vibration of the $Cr=^{18}O$ bond. When norbornene is introduced, the epoxide containing 94% of ^{18}O is formed. Special experiments demonstrated that PhIO is not involved in oxygen exchange with $H_2^{18}O$ under these conditions.

Analogous results have been obtained in the presence of TPhP-MnCl[130] and TMP-FeCl (TMP is the tetramesitylporphin ligand).[141] In addition, a reliable instance of the transfer of an oxygen atom to the substrate undergoing oxidation from an oxo-metalloporphyrin is known. This is the reaction involving the oxidation of substituted phosphine by *cis*-dioxomolybdenum(VI)-tetra-*p*-tolylporphin:[146,147]

$$T\,(p\text{-}CH_3\text{-}Ph)\,P\text{-}Mo^{VI}\!\!\begin{matrix}O\\O\end{matrix} + PR_3 \rightarrow T\,(p\text{-}CH_3\text{-}Ph)\,P\text{-}Mo^{IV}{=}O + OPR_3.$$

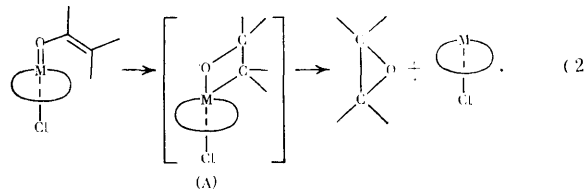
It has been shown recently[148] that the imido-complex of Mn-porphyrin effects direct oxidative amination of olefins, which leads to nitrogen-containing analogues of epoxides.

The oxo-complexes of metalloporphyrins formed when P-MCl interacts with iodosobenzene in solution in methylene chloride have been isolated at reduced temperatures; their structure and properties have been characterised by various methods (infrared, EPR, NMR, and Mössbauer spectroscopy, the spectroscopy in the visible region, and measurements of magnetic susceptibility.[128-131,140,141,149] The oxo-complex of chromium is stable at room temperature for several hours.[129] In the solid state the oxo-complex of manganese is stable for several days at 25 °C, but, on dissolution in aromatic and chlorinated hydrocarbons, it is rapidly reduced with formation of P-Mn^{3+}Cl.[130,131] Solutions of oxo-complexes of iron are unstable at room temperature.[140,141]

The entire set of data shows that the oxo-complexes of chromium and manganese contain a quintuply charged metal ion: Cl(TPhP)Cr^{5+}=O and Cl(TPhP)Mn^{5+}=O. However, it has been suggested[145] that, when TPhP-MnOAc reacts with iodosobenzene in solution in methanol, the oxo-complex of quadrivalent manganese, i.e. TPhP-Mn^{4+}=O, is formed. Study of the structure of the oxo-complex of iron,[141,150] permits the conclusion that it contains quadrivalent iron and the radical-cation derived from the porphyrin ligand: Cl(TMP)$^{\cdot}$. .Fe^{4+}=O. Although this structure does not in fact account for all the observed spectroscopic properties, it agrees with the results of a study[151] showing that the electrochemical oxidation of TPhPFe^{4+}(Cl)(OH) involves the porphyrin ligand and not the central metal ions; the process results in the formation of (TPhP)$^{\cdot}$Fe^{4+}(Cl)(OH). This behaviour of Fe-porphyrin arises because, according to theoretical calculations,[152] the energies of the lowest *d* orbitals of the iron ion and the a_{2u} orbitals of the TPhP ligand are similar. The energies of the *d* orbitals of the chromium and manganese ions are higher than those of the a_{2u} orbitals of TPhP and these complexes are therefore oxidised with participation of the central metal ion. It is noteworthy that the spectrum of the oxo-complex of iron, obtained by Groves et al.,[141] is analogous to that of compound I of horseradish peroxidase.

The mechanisms of oxygen transfer from the oxo-complexes of Mn-porphyrin, on the one hand, and Cr- and Fe-porphyrins, on the other, are apparently different. The PhIO–P-CrCl (or P-FeCl) oxidising system is characterised, apart from the features described above, also by a high specificity of the reaction in relation to *cis*-olefins, which indicates a major role of steric factors. Thus the PhIO–TPhP-FeCl system oxidises a mixture of *cis*- and *trans*-stilbenes with formation of only *cis*-stilbene oxide in 80% yield; *cis*-but-2-ene is six times more reactive than *trans*-but-2-ene; *cis*, *trans*, *trans*-cyclododecatriene gives rise to a 2:1 mixture of the *trans*- and *cis*-epoxides (i.e. the reactivities of both types of bonds are approximately the same), while the oxidation of this compound by *m*-chloroperbenzoic acid results in the formation of 98% of the *trans*-isomer.[129] In addition, data have been obtained[128] showing an increase of the reactivity of olefins with increasing nucleophilicity of the double bond (the reaction rates increase in the sequence stilbene < styrene < norbornene).

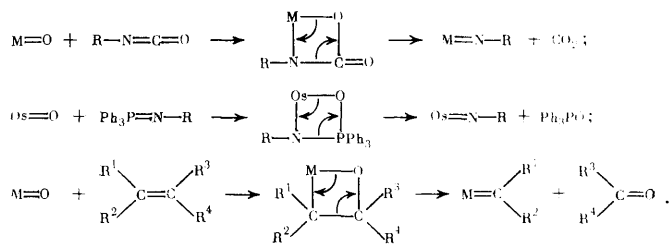
Taking into account all these features, one can put forward the following mechanism of the transfer of an oxygen atom from the oxo-complexes of Cr- and Fe-porphyrins to olefins. In the first stage an olefin molecule is coordinated to the central metal ion of the oxo-complex, after which the olefin is inserted in the metal–oxygen bond, with formation of a four-membered cyclic intermediate complex (A), which then disproportionates to the epoxide and a metalloporphyrin, the latter entering a new catalytic cycle:



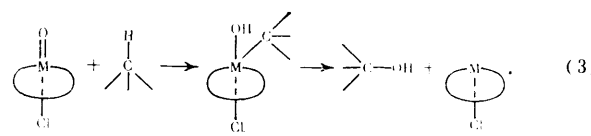
(2)

(A)

The formation of four-membered transition states has been postulated in a number of reactions of the oxo-complexes of metals,[102] including isocyanates, phosphine imines, and olefins:



The mechanism of the oxidation of saturated hydrocarbons by the oxo-complexes of Fe- and Cr-porphyrins can be represented analogously. The heterolytic cleavage of the C–H bond leads simultaneously to the rupture of the metal–oxygen bond. The complex (B) formed as a result of the reaction then decomposes into an alcohol and the metalloporphyrin:



(3)

(B)

It is difficult to account for the characteristic features of the cyclohexene oxidation reaction in the presence of Fe- and Cr-porphyrins, which deviates from this picture. An alcohol and even a ketone are formed together with the epoxide in the presence of Fe- and Cr-porphyrins, the proportions of the products being different in the two cases (Table 2). It may be that the competitive activation of the double bond [reaction (2)] and the allyl C–H bond [reaction (3)] takes place and the contributions of these reactions depend significantly on the nature of the metal in the oxo-complex.

According to the proposed mechanisms of the oxidation of olefins and alkanes by the oxo-complexes of Fe- and Cr-porphyrins, the transition complexes (A) and (B) are formed via reactions (2) and (3) without changes in the oxidation state of the metal ion but with dissociation of the M=O bond. Consequently the M=O bond in the porphyrin complex must be fairly labile in relation to heterolytic cleavage for reactions (2) and (3) to occur. There is reason to suppose that the M=O bond in the complex Cl(TPhP)Mn=O is more stable than in the corresponding iron and chromium complexes. The Mn^{5+} ion is apparently more electrophilic than the Cr^{5+} ion, since the Mn^{5+} radius should probably be smaller than the Cr^{5+} radius (in view of the lack of data for the dimensions of these ions owing to their extreme instability, we shall quote for the purposes of the comparison the radii of the Mn^{3+} and Cr^{3+} ions, which are respectively 0.62 and 0.64 Å or 0.68 and 0.71 Å.[153] Consequently the Mn^{5+}=O bond should be stronger than the Cr^{5+}=O bond. This is confirmed by the infrared spectroscopic data for the corresponding oxo-porphyrin complexes of manganese and chromium. The

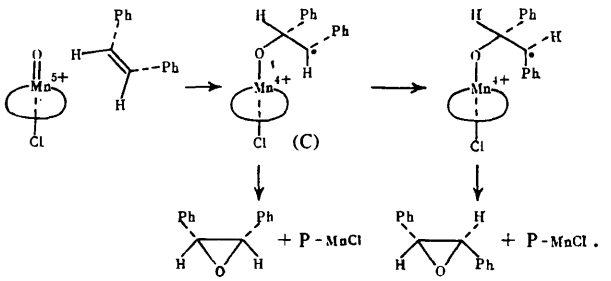
higher absorption frequency corresponding to the vibrations of the Mn=O group (ν = 1060 cm^{-1})[143] compared with the Cr=O group (ν = 1026 cm^{-1})[126,127] shows that the Mn=O bond is stronger and shorter. The quadrivalent iron ion present in the complex $Cl(TPhP)^{+}Fe^{4+}=O$ is less electrophilic than the quinquevalent manganese ion and the $Fe^{4+}=O$ bond is therefore stronger than the $Mn^{5+}=O$ bond. Although there are no infrared spectroscopic data for the vibration frequency of the $Fe^{IV}=O$ bond, the higher activity of $Cl(TPhP)^{+}Fe^{IV}=O$ compared with $Cl(TPhP)Cr^{V}=O$ in the olefin epoxidation reaction (Table 2), suggests that the $Fe^{IV}=O$ bond is more labile than the $Cr^{V}=O$ bond.

In the Cr^{5+}, Mn^{5+}, Fe^{4+} series, the best oxidant should be the manganese ion, which is indicated by the calculated ionisation potentials (the following ionisation potentials correspond to the $M^{4+} - e \rightarrow M^{5+}$ process: 76V for M = Mn and 73 V for M = Cr; 56 V for the process $Fe^{3+} - e \rightarrow Fe^{4+}$.[154] (The oxidation-reduction potentials of the corresponding porphyrin complexes have not been determined.) This suggests that there is a possibility of the reduction of quinquevalent manganese in the oxo-complex which leads to a radical species. This can be represented conventionally in the following manner:

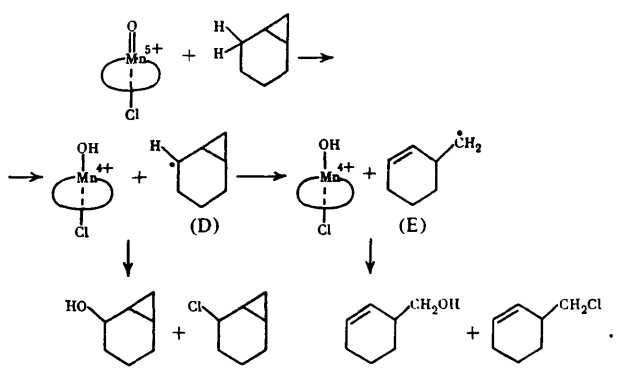
$$TPhP\text{-}Mn^{5+}\quad O \cdots TPhP\text{-}Mn^{4+}\cdots O\cdot .$$

Apparently these distinctive properties of the oxo-complex of Mn-porphyrin actually determine the radical mechanism of the transfer of an oxygen atom to the substrate undergoing oxidation, a characteristic feature of which is a change in the oxidation state of manganese on formation of the transition complex.

The homolytic rupture of the double bond of the olefin occurring in the reaction with (Cl)TPhP-Mn=O leads to the radical intermediate (C), the free rotation about the C–C bond in which is apparently responsible for the formation of a mixture of *cis*- and *trans*-isomeric products in the oxidation of *cis*-stilbene.[130]



On interaction with saturated hydrocarbons, the oxo-complex of the Mn-porphyrin apparently abstracts from them a mobile hydrogen atom. A tentative reaction mechanism is presented below for norcarane:[130]

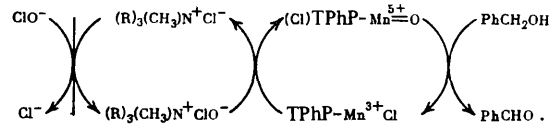


The norcaranyl free radical (D) formed can subsequently abstract one of the axial ligands from the complex TPhP-Mn.(Cl)(OH) or a chlorine atom from the chlorinated solvent and can also rearrange to the radical (E). The reactions of the radical (D) via several pathways are in fact responsible for the large assortment of reaction products.

It is seen from the foregoing that the specificity of the action of metalloporphyrins in the oxidation of hydrocarbons by iodosobenzene depends significantly on their structure and in particular on the nature of the central metal ion: thus, whereas Fe- and Cr-porphyrins catalyse selective oxidation, Mn-porphyrin initiates a radical process.

IV. REACTIONS OF ORGANIC COMPOUNDS WITH SODIUM HYPOCHLORITE

Metalloporphyrins are also effective catalysts of the oxidation of organic compounds by sodium hypochlorite in immiscible solvents in the presence of a phase transfer agent[155–158] (Table 3). The use of a porphyrin catalyst combined with a phase transfer agent gives rise to a powerful synergistic effect. Table 4 shows that, in the absence of one of the components of the catalytic system, the rate of oxidation of benzyl alcohol is appreciably reduced. The function of the phase transfer agent consists in transporting the oxidising ion ClO^{-} from the aqueous phase to the organic phase containing the substrate to be oxidised,[155] where the catalytic process actually takes place:



This oxidising system is very effective in the oxidation of alcohols and ethers to the corresponding aldehydes. Saturated hydrocarbons and olefins are oxidised fairly rapidly; for example, the degree of conversion of styrene in the presence of TPhP-MnOAc is 68% in 1 h,[156] the epoxide and other products being formed (Table 3).

The mechanism of the oxidation reaction involving sodium hypochlorite has not been investigated hitherto. However, one may suppose that it proceeds via the intermediate formation of the oxo-complex of the metalloporphyrin. Thus it has been shown[145] that the interaction of TPhP-MnOAc with NaClO results in the formation of a compound whose spectrum is analogous to that of the product of the reaction of TPhP-MnOAc with PhIO. Furthermore, the presence of chlorinated alkanes in the products of the oxidation of saturated hydrocarbons by the TPhP-MnCl–NaClO system[155] as well as the complete suppression of the reaction in the presence of the radical inhibitor 2,6-di-t-butyl-*p*-cresol[155] indicate a radical mechanism of the reaction. A similar mechanism is also characteristic of the TPhP-MnCl–PhIO system, which suggests that the active species involved in the two systems are identical.

V. THE INTERACTION OF OLEFINS WITH HYDROPEROXIDES AND PERACIDS

The reactions involving oxidation by hydroperoxide compounds and peracids in the presence of metalloporphyrins and metallophthalocyanines[133,136,141,159–168] (Tables 5–7) apparently proceed with participation of active species of a different kind than in the case of iodoso-compounds and sodium

Table 3. Oxidation of organic substrates by sodium hypochlorite in immiscible solvents in the presence of metalloporphyrin catalysts and a phase transfer agent at 25 °C.

Substrate	Catalyst	Solvent	Phase transfer agent	τ, min	Products	W, %	χ, %*	Refs.
Styrene	TPhP-MnOAc	CH_2Cl_2:H_2O = 2:1	BMDAC	180	Styrene oxide Other products	45 55	80 (3200)**	[156]
Styrene***	TPhP-MnOAc	CH_2Cl_2:H_2O = 1:2	BMDAC	30	Styrene oxide Other products	80 20	100 (16 000)**	[158]
Styrene	TPhP-FeCl	CH_2Cl_2:H_2O = 2:1	BMDAC	180	Styrene oxide Other products	6 94	33 (1340)**	[156]
Styrene	TPhP-CoBr	CH_2Cl_2:H_2O = 2:1	BMDAC	180	Styrene oxide Other products	11 89	53 (2120)**	[156]
Cyclohexene	TPhP-MnOAc	CH_2Cl_2:H_2O = 2:1	BMDAC	180	Epoxycyclohexane Other products	21 79	70 (2800)**	[156]
Cyclohexene****	TPhP-MnOAc	CH_2Cl_2:H_2O = 1:2	BMDAC	240	Epoxycyclohexane Other products	85 15	95 (15 200)**	[158]
Cyclohexane	TPhP-MnCl	CH_2Cl_2:H_2O = 3:2	TOMAC	20	Cyclohexanone Cyclohexyl chloride	5 95	80 (1155)	[155]
Adamantane	TPhP-MnCl	CH_2Cl_2:H_2O = 3:2	TOMAC	200	1-Chloroadamantane 1-Adamantanol 2-Chloroadamantane 2-Adamantanol 2-Adamantanone	47 17 21 11 4	20 (430)**	[155]
Benzyl alcohol	TPhP-MnCl	CH_2Cl_2:H_2O = 3:2	TOMAC	5	Benzaldehyde	—	94 (150)	[155]
Dibenzyl ether	TPhP-MnCl	CH_2Cl_2:H_2O = 3:2	TOMAC	1	Benzaldehyde	—	85 (189)	[155]
Benzyl isopropyl ether	TPhP-MnCl	CH_2Cl_2:H_2O = 3:2	TOMAC	1	Benzaldehyde	—	79 (239)	[155]

Notation: BMDAC = benzyldimethyltetradecylammonium chloride; TOMAC = trioctylmethylammonium chloride.

*Yield relative to the substrate oxidised; the yield relative to the catalyst is given in brackets.
**Yield relative to the catalyst calculated by ourselves from authors' data.
***In the presence of added pyridine.
****In the presence of added 4-methylpyridine.

hypochlorite. This is indicated, in particular, by the dependence of the proportions of the oxidation products on the nature of the oxidant (Table 7). In addition, according to Groves et al.,[141] the interaction of tetramesitylporphinatoiron chloride (TMP.FeCl) with perbenzoic acid and iodosobenzene results in the formation of compounds of different nature, manifesting different reactivities in the epoxidation of olefins.

It has been suggested recently that the reactions involving the transfer of oxygen from peroxy-compounds to the substrate being oxidised, catalysed by cytochromes P-450, proceed via the formation of a cytochrome–peroxy-compound complex.[169-171]

Table 4. The rate constants for the oxidation of benzyl alcohol in immiscible solvents (CH_2Cl_2 : H_2O = 3 : 2) at room temperature.[155]

Oxidising system	$10^3 d[PhCHO]/dt$, mol litre min^{-1}	k
NaClO*	1.5	0.0083 litre mol^{-1} min^{-1}
NaClO + TOMAC	4.5	0.930 litre^2 mol^{-2} min^{-1}
NaClO + TPhP-MnCl	4.4	1.460 litre^2 mol^{-2} min^{-1}
NaClO + TOMAC + TPh-MnCl MnCl	65	375 litre^3 mol^{-3} min^{-1}

*3.6×10^{-4} mol of NaClO in a mixture of 3 ml of CH_2Cl_2 and 2 ml of an aqueous solution of alkali (pH 12.8).

Table 5. Selectivity of the epoxidation of olefins by hydroperoxides and peracids in the presence of various metalloporphyrin and metallophthalocyanine catalysts.

Olefin	Catalyst	Oxidant	W_e, %	Refs.
Cyclohexene	(Py)(Cl)(TPhP) Mo = O	$(CH_3)_3COOH$*	68	[159]
Cyclohexene	(CH_3O)(TPhP) Mo = O	$(CH_3)_3COOH$*	84	[159]
Cyclohexene	TPhP-MoO_2	$(CH_3)_3COOH$*	85	[159]
Cyclohexene	Pc-MoO_2	$(CH_3)_3COOH$	>90	[160]
Oct-1-ene	Pc-MoO_2	$(CH_3)_3COOH$	>90	[160]
Cyclohexene	T(*p*-CH_3O-Ph) P-FeCl	$(C_6H_5)(CH_3)_2COOH$	<1	[161]
Cyclohexene	T(*p*-CH_3O-Ph) P-FeCl	(*m*-Cl-C_6H_4)CO_3H	<1	[161]
Cyclohexene	T(*p*-CH_3O-Ph) P-FeCl	(*p*-NO_2-C_6H_4)CO_3H	<1	[161]

Notation: Pc = phthalocyanine ligand; W_e = content of epoxide in products.
*In benzene at 80 °C.

In the selective epoxidation of cyclohexene, *cis*- and *trans*-hex-2-enes, and isoprene with t-butyl hydroperoxide in the presence of the Cl(TPhP)Mo^{V}=O catalyst, towards the end of the induction period a complex was detected in the system by spectroscopy in the visible region, to which the structure (t-Bu–O–O)(TPhP)Mo=O was attributed.[159]

All these factors suggest that the first stage in the oxidation of hydrocarbons by hydroperoxides and peracids in the presence of metalloporphyrins and metallophthalocyanines is the formation of a catalyst–oxidant complex:

$$P\text{-}M^{n+} + ROOH \rightleftarrows [P\text{-}M^{n+}\cdot ROOH].$$

Such complexes have been described in the literature – these are the complexes of tetra(*p*-methoxyphenyl)porphinatoiron chloride T(*p*-CH_3O-Ph)P-FeCl with cumenyl hydroperoxide and substituted perbenzoic acids,[161] of T(p-X-Ph)P-Co (X = OCH_3, H, or Cl) with 1,2,3,4-tetrahydro-1-naphthyl, 1-methyl-1-phenylethyl, and t-butyl hydroperoxides,[172] of tetramesitylporphinatomanganese chloride with *m*-chloroperbenzoic acid,[173] and of Pc-Cu with cumenyl hydroperoxide.[174] In the last case it is assumed that the copper ion is not directly involved in the formation of the complex and that the complex formation reaction proceeds via the phthalocyanine ligand.[175]

The porphyrin and phthalocyanine complexes of molybdenum exhibit a high selectivity and stereospecificity in the epoxidation of olefins by hydroperoxides[159,160] (Table 5): the epoxidation of *cis*- and *trans*-hex-2-ene by t-butyl hydroperoxide in the presence of Cl(TPhP)Mo=O results in the formation of 97 and 99% of the *cis*- and *trans*-2,3-epoxides respectively;[159] the rate of epoxidation then depends on the nature of the olefin and increases with increasing nucleophilicity of the double bond.[160] On the other hand, in the presence of Fe-porphyrin catalysts the oxidation of olefins by hydroperoxides and peracids leads to the preferential formation of allyl oxidation products – unsaturated alcohols and ketones, and the content of epoxides is less than 1%[161] (Table 6).

Table 6. Dependence of the proportions of the cyclohexene oxidation products on the nature of the oxidant (catalyst–tetra-*p*-methoxyphenylporphinatoiron chloride).[161]

Oxidant	Proportions of products, %		
	epoxycyclohexane	cyclohex-2-en-1-one	cyclohex-2-en-1-ol
$(C_6H_5)(CH_3)_2CO_2H$	1	18	81
$(m\text{-}Cl-C_6H_4)CO_3H$	1	59	40
$(p\text{-}NO_2-C_6H_4)CO_3H$	1	51	49
C_6H_5IO	20	12	67

The complex of the metalloporphyrin or metallophthalocyanine with the hydro-peroxy-compound formed in the reaction system is converted via two pathways. On the one hand, it can epoxidise the olefin via a heterolytic mechanism (the oxidation state of the central metal ion does not change):

$$[P\text{-}M^{n+} \cdot ROOH] + \text{>C=C<} \rightarrow \text{>C(O)C<} + ROH + P\text{-}M^{n+}, \quad (4)$$

and, on the other hand, there is a possibility of the homolytic decomposition of the hydroperoxide via the following oxidation-reduction process:

$$[P\text{-}M^{n+} \cdot ROOH] \rightarrow P\text{-}M^{(n-1)+} + RO_2^{\cdot} + H^+, \quad (5)$$

followed by the oxidation of the olefin via a radical mechanism.

It is noteworthy that a homolytic oxidation pathway is postulated together with the heterolytic pathway in the reactions involving the oxidation of organic substrates by hydroperoxides and peracids and catalysed by cytochromes P-450.[40,45,115,176–179]

The selectivity of the epoxidation of olefins is determined by the relative contributions of the two competing pathways (4) and (5). The ratio of the Lewis acidity and oxidising capacity of the central metal ion determines its preferential involvement in a particular reaction. The more pronounced are the acidic properties of the metal ion the higher is the activity which it should exhibit in the heterolytic epoxidation reaction [reaction (4)] and the higher its oxidation-reduction potential the more effective should be its involvement in reaction (5). Electron-accepting substituents in the porphin ring of the catalyst and electron-accepting *trans*-ligands should enhance the acid properties of the central metal ion and hence should increase the activity of the catalyst in reaction (4).

Table 7. Dependence of the proportions of cyclohexane oxidation products on the nature of the oxidant.

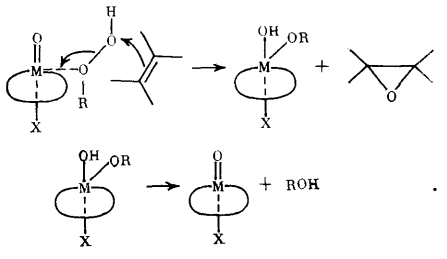
Catalyst	Oxidant	Proportions of products, %		Overall yield, %	Refs.
		cyclohexanol	cyclohexanone		
TPhP-FeCl	$(CH_3)_3CO_2H$	66.5	33.5	32	[162]
TPhP-FeCl	$(C_6H_5)(CH_3)_2CO_2H$	67	33	60	[162]
TPhP-MnCl	$(C_6H_5)(CH_3)_2CO_2H$	67.5	32.5	37	[133]
TPhP-CoCl	$(C_6H_5)(CH_3)_2CO_2H$	66.5	33.5	60	[133]
TPhP-CrCl	$(C_6H_5)(CH_3)_2CO_2H$	72	28	46	[133]
TPhP-FeCl	C_6H_5IO	92	8	13	[162]
TPhP-MnCl	C_6H_5IO	91	9	33	[133]
TPhP-CrCl	C_6H_5IO	50	50	8	[133]
TPhP-CoCl	C_6H_5IO	77	23	6.5	[133]

*Relative to the oxidant.

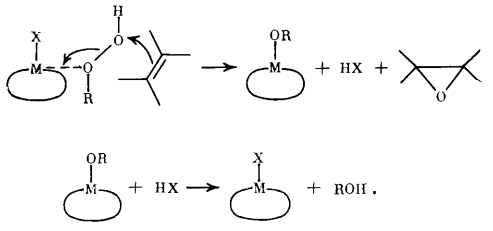
The higher selectivity of the epoxidation of olefins in the presence of the oxomolybdenum complexes of porphyrins and phthalocyanine compared with the Fe-porphyrin complexes (Table 5) is apparently associated with the fact that the Mo^{5+} ion, linked to the electron-accepting oxo-group, possesses a much higher Lewis acidity than tervalent iron (according to theoretical calculations,[180] the effective charge on the iron ion in TPhP-FeCl is +0.27).

Oxomolybdenumporphyrins and oxomolybdenumphthalocyanines also catalyse the radical oxidation of olefins by a hydroperoxy-compound; this is indicated by the fact that the selectivity of the epoxidation is not 100% (Table 5). This finding agrees with the fairly high oxidising capacity of the catalyst–$E_{1/2}(Mo^{5+}/Mo^{4+})$ = +0.11 V relative to the saturated calomel electrode has been obtained for (OH).(TPhP)Mo=O in DMF[181] [under the same conditions, $E_{1/2}$.(Fe^{3+}/Fe^{2+}) = −19 V [sic] for TPhP-FeCl [181]]. Fe-porphyrins catalyse preferentially the homolytic cleavage of the peroxide linkage [reaction (5)] and are almost inactive in the epoxidation reaction [reaction (4)].

By analogy with the mechanism of the action of molybenum oxide and vanadium oxide catalysts,[160,182–185] the mechanism of the transfer of peroxide oxygen from the complex P-M.ROOH to the olefin can be represented as follows. The function of the catalyst consists in displacing the electron density from the peroxide oxygen atoms, which increases the electrophilicity of the hydroperoxide and thus activates it with respect to the electrophilic attack by the olefin double bond:



The oxo-group of the catalyst fulfills the role of an intramolecular proton acceptor. In the absence of the M=O group, this role is apparently assumed by the axial ligand.



The olefin is apparently not coordinated to the metal ion of the catalytic centre. The reactivity of olefins having bulky substituents is determined mainly by steric factors and not by the nucleophilic properties of the double bond. Thus the epoxidation of isoprene by t-butyl hydroperoxide in the presence of (Cl)(TPhP)Mo=O results in the formation of 3,4-epoxy-3-methylbut-1-ene and 3,4-epoxy-2-methylbut-1-ene in proportions of 0.7 : 1.0, whereas in the reaction where $Mo(CO)_6$ is used as the catalyst the ratio is 4 : 1.[159] Similar steric effects have been noted in the oxidation of phosphines in the presence of TPhP.MoO_2: it has been shown that the rate constant is sensitive not to the electron-donating properties of the substituents R in the PR_3 molecule but to their size.[146]

According to kinetic data,[160] the reactions involving the epoxidation of cyclohexene and oct-1-ene by t-butyl hydroperoxide in the presence of Pc-MoO_2 in methylcyclohexane are of first order with respect to the hydroperoxide, the olefin, and the catalyst, i.e. epoxidation in accordance with reaction (4) takes place preferentially in the system. Apparently, apart from the fact that Pc-MoO_2 exhibits only a weak activity in reaction (5), the homolytic decomposition of the hydroperoxide is inhibited by the olefin and the solvent.

After the formation of the primary radical via reaction (5), the hydroperoxide decomposition process proceeds via the following mechanism:

$$2RO_2^{\cdot} \rightarrow 2RO^{\cdot} + O_2;\ RO^{\cdot} + RO_2H \rightarrow ROH + RO_2^{\cdot}.$$

In the presence of a solvent SH containing active C–H bonds or of an olefin, the kinetic hydroperoxide decomposition chain terminates:[160]

$$RO^{\cdot}(RO_2^{\cdot}) + SH \rightarrow ROH(RO_2H) + S^{\cdot},$$
$$S^{\cdot} + RO_2^{\cdot} \rightarrow SO_2R \rightarrow \text{products},$$
$$S^{\cdot} + O_2 \rightarrow SO_2^{\cdot} \rightarrow \text{products},$$

or

$$RO^{\cdot}(RO_2) + -CH_2-CH=CH_2 \rightarrow ROH(RO_2H) + -\dot{C}H-CH=CH_2,$$
$$-\dot{C}H-CH=CH_2 + RO_2^{\cdot} \rightarrow -CH(O_2R)-CH=CH_2 \rightarrow \text{products},$$
$$-\dot{C}H-CH=CH_2 + O_2 \rightarrow -CH(O_2^{\cdot})-CH=CH_2 \rightarrow \text{products}.$$

Indeed the rate of decomposition of t-butyl hydroperoxide in benzene and chlorobenzene is 8 times higher than in cyclohexane and methylcyclohexane.[160]

The formation of the products of the allyl oxidation of olefins, characteristic of catalysts active in the homolytic decomposition of hydroperoxide [reaction (5)], can be represented as follows:

$$-CH(O_2R)-CH=CH_2 \xrightarrow{\text{catalyst}} -CH(\dot{O})-CH=CH_2,$$
$$2-CH(\dot{O})-CH=CH_2 \rightarrow -\underset{\underset{O}{\|}}{C}-CH=CH_2 + -CH(OH)-CH=CH_2.$$

It is known that peracids effectively epoxidise unsaturated hydrocarbons.[186,187] Thus the selectivity of the epoxidation of cyclohexene by *m*-chloro- and *p*-nitroperbenzoic acids via the stoichiometric reaction is very high, amounting to 82–92% (Table 8). The introduction of the Fe-porphyrin catalyst into the system alters sharply the composition of the oxidation product and lowers their epoxide content to 1%. This is associated with the fact that the active decomposition of the peracids via reaction (5) in the presence of T(OCH_3-.Ph)P-FeCl suppresses the epoxidation reaction.

Table 8. Proportions of the products of the oxidation of cyclohexene by peracids.[161]

Catalyst	Oxidant	Yield*, %	Proportions of products, %		
			epoxycyclohexane	cyclohex-2-en-1-one	cyclohex-2-en-1-ol
—	(*m*-Cl—C_6H_4)CO_3H	63	92	3	4
	(*p*-NO_2—C_6H_4)CO_3H	86	82	9	8
T(*p*-CH_3O-Ph)P-FeCl	(*m*-Cl—C_6H_4)CO_3H	60	<1	59	40
T(*p*-CH_3O-Ph)P-FeCl	(*p*-NO_2—C_6H_4)CO_3H	56	<1	51	49

*Relative to the oxidant.

Table 9. The yield* (%) of the products of the oxidation of cyclohexane by cumenyl hydroperoxide.[162]

Catalyst	TPhP-CoCl	TPhP-FeCl	THp-MnCl	TPhP-Os(CO)(Py)
Cyclohexanol	45	40	1	5
Cyclohexanone	23	20	0.5	2.5

*Relative to the hydroperoxide.

According to Mansuy and coworkers,[133,162] TPhP-FeCl, TPhP-CoCl, and TPhP-RhI effectively catalyse the oxidation of cyclohexane by cumenyl hydroperoxide with formation of cyclohexanol and cyclohexanone in proportions of 2 : 1. (CO)(Py)(TPhP)Os, TPhP-CrCl, and TPhP-MnCl show a lower activity in this reaction, while Cu^{II}-, Ni^{II}-, Zn^{II}-, and Mg^{II}-TPhP, TPhP-V^{IV}=O, and TPhP-Ti^{IV}=O are inactive (Table 9). It has been observed that Fe-porphyrins catalyse the oxidation of n-heptane by cumenyl hydroperoxide[133] with formation of alcohols and ketones. Presumably in these systems, the hydroperoxide undergoes homolytic decomposition via reaction (5) with subsequent involvement of cyclohexane and n-heptane in the radical process. This is indicated by a number of factors – the rapid decomposition of cumenyl hydroperoxide at the beginning of the reaction[162] and the activity of only those catalysts whose central metal ion is capable of undergoing a change in the oxidation state, which is essential for the occurrence of reaction (5). Indeed the central metal ion is involved in the oxidation-reduction cycles of Cr-, Mn-, Fe-, Co-, and Os-porphyrins, while the oxidation-reduction of Cu-, Zn-, Mg-, TiO-, and VO-porphyrins involves the porphyrin ring. In the case of TPhP-Ni the Ni^{2+} ion and the TPhP ligand are oxidised at the same potential (Table 10); according to Yamada and Kamiya,[172] TPhP-Ni and TPhP-Cu do not form complexes with hydroperoxides. Furthermore, the increase of the activity of the catalysts containing a tervalent metal ion with increase of their oxidising

capacity is consistent with the proposed homolytic decomposition of the hydroperoxide, i.e. TPhP-MnCl < TPhP-FeCl < TPhP-CoCl (Table 10).

Table 10. Oxidation-reduction potentials of metalloporphyrins ($E_{1/2}$, V)*.[181]

Compound	Oxidation of ring		Metal	Reduction of ring	
	$-2\bar{e}$	$-\bar{e}$		$+\bar{e}$	$+2\bar{e}$
TPhP-CrCl	—	—	III/II—1.06	—1.69	—1.91
TPhP-MnCl	—	—	III/II—0.23	—1.52	
TPhP-FeCl	—	1.4**	III/II—0.19	—1.61	—
TPhP-Co	1.26	1.06	II/III+0.32	—1.87	—
TPhP-Ni	1.40	1.10	II/III+1.04	—1.18	—1.75
TPhP-Cu	1.16	0.90	—	—1.20	—1.68
TPhP-Zn	1.03	0.71	—	—	—1.80
TPhP-Mg	0.86	0.54	—	—1.35	—1.80
OEP-Ti = O	1.32	1.03	—	—1.21	—1.69
TPhP-V = O	1.22	1.00	—	—0.94	—1.32
OEP-Os(CO)(Py)	—	—	II/III+0.48	—	—

*Potentials relative to the saturated calomel electrodes; reduction in DMF or dimethyl sulphoxide; oxidation in CH_2Cl_2 or butyronitrile.
**Irreversible oxidation.

Thus the mechanism of the oxidation of olefins by hydroperoxides is determined by the nature of the metalloporphyrin or metallophthalocyanine catalyst – the acid and oxidation-reduction properties of the central metal ion determine the reaction pathway, which involves either the activation of the hydroperoxide for electrophilic attack on the olefin or the homolytic decomposition of the hydroperoxide and subsequent free-radical oxidation of the olefin.

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In conclusion, it must be emphasised that the presence in metalloporphyrin molecules of a central metal ion in different oxidation states and having in the *d* shell electrons with unpaired spins together with a planar porphyrin ligand having an extensive π-conjugation system gives rise to the possibility of a wide variety of different types of action by metalloporphyrins in reactions involving the oxidation of organic compounds by molecular oxygen and oxygen-containing oxidants: they can catalyse a selective oxidation reaction and can initiate free-radical oxidation.

The behaviour of metalloporphyrins in oxidation reactions depends very greatly on their structure, i.e. on the nature of the central metal ion and the porphyrin ligand. In particular, the replacement of the metal ion can alter radically the mechanism of the oxidation of organic substrates by oxygen-containing compounds.

Strictly speaking, metalloporphyrins are not true catalysts of the selective oxidation of organic compounds by molecular oxygen because a reductant is necessary for the regeneration of the catalyst and the completion of the catalytic cycle.

The reactions involving the epoxidation of olefins by iodosobenzene, sodium hypochlorite, and hydroperoxides, and other oxygen donors[188] in the presence of certain metalloporphyrins and phthalocyanines do not require a reductant and they can be regarded as truly catalytic.

The proposed mechanisms of the selective oxidation of organic substrates by molecular oxygen and iodosobenzene presuppose the formation of the peroxo- or oxo-complex of the metalloporphyrin respectively, the coordination of the substrate being oxidised to the metal ion in this complex, and its subsequent insertion in the metal-peroxo or metal-oxo bond. The porphyrin ligand apparently plays the very important role of an electron "buffer", stabilising the transition states of the catalytic process.

It is significant that the nature of the reductant determines the composition of the products of the oxidation of olefins by molecular oxygen. When weak reducing agents are used, the corresponding epoxy-derivatives are formed. Strong reductants effect the reductive cleavage of the M–C and O–O bonds in the cyclic intermediate complex, which leads to the formation of saturated alcohols and ketones.

From the standpoint of the solution of the problem of the creation of new catalytic systems for mild selective oxidation, we believe it is useful to investigate reactions involving the oxidation of organic compounds by molecular oxygen in the presence of metalloporphyrins and reductants. The choice of a suitable reductant is then crucial, since it determines the nature of the resulting oxidation product.

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New Spectroscopic Methods in Gas-Phase Chemical Kinetics

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The possibilities provided by the application of advances in laser technology to the solution of problems in gas-phase chemical kinetics have been analysed. The basic principles of various laser methods for producing and recording active chemical species have been described. Examples of the use of lasers to study the reactions of radicals and excited species, in the diagnostics of complex chemical processes, and to carry out selective laser-chemical reactions have been examined.
The bibliography contains 110 references.

CONTENTS

I. Introduction 231
II. Methods of laser spectroscopy 232
III. The use of lasers in gas-phase chemical kinetics 235

I. INTRODUCTION

Particular attention has been paid to different problems at various stages of the development of gas-phase chemical kinetics, depending on the state of the theory, practical requirements, and available methods of study. In recent years, a qualitative leap has been made in physicochemical methods of study. The production of lasers, particularly tunable lasers, has made it possible to develop effective methods both for studying a chemical reaction and for influencing it. These methodological possibilities have not only raised studies in traditional directions to a qualitatively higher level but have also defined new and promising problems in gas-phase chemical kinetics.

From the beginning of the development of gas-phase chemical kinetics, two main directions have existed: the study of the general regular features of the course of complex chemical reactions and the study of the elementary steps. The study of complex chemical reactions has shown that most of them consist of a set of elementary steps involving extremely reactive intermediate species — radicals. The general regular kinetic features of radical, chain, and chain branched reactions have been established. These general regular features have been demonstrated for oxidation, halogenation, and cracking reactions. A fundamental contribution to the development of this field was made by Semenov's general theory of chain reactions.[1,2]

The course of a chemical reaction is influenced considerably not only by the active species but also by the energy liberated in the exothermic elementary stages. Allowance for the liberated energy has led to the establishment of the regular features of the non-isothermal course of a reaction. A theory of thermal self-ignition has been developed.[2,3] In these theories, however, it has been assumed that the energy is liberated as heat, and that it can be characterised by a single temperature for all degrees of freedom.

Analysis of all the established regular features has shown that the study of complex chemical reactions cannot be restricted to kinetic measurements of the concentrations of stable species, but must include the recording of the radicals driving the reaction chain and the quantitative study of elementary reactions. The need for quantitative data on elementary reactions is increasing continuously, due to the increasing demands of practice, which requires increasingly reliable quantitative information on the mechanisms of chemical processes.

At the present time there are comparatively simple and general theoretical approaches for calculating the rate constants of elementary reactions taking place under the conditions of Maxwell–Boltzmann energy distribution for the species. These are the transition state method for direct bimolecular reactions and the statistical theory of unimolecular reactions (RRKM theory) and bimolecular reactions, which essentially uses the ideas of the transition state method. These theories give explicit expressions for reaction rate constants in terms of the parameters of the potential energy surfaces.[4-6] The accuracy with which these parameters are known is quite inadequate, however, so that the experimental determination of the rate constants of elementary reactions remains an important problem in gas-phase chemical kinetics.

The subsequent development of the theory of gas-phase chemical kinetics is related to the fact that different forms of the energy of molecules (translational, rotational, vibrational, and electronic excitation energy) are not equivalent from the viewpoint of overcoming the activation barrier. A large number of studies have shown that the breakdown of the Maxwell–Boltzmann distribution of the energy with respect to different degrees of freedom of the reacting species may have a significant influence on the course of a reaction. One clear example of this is provided by the discovery of the class of reactions with energy branching.[7-9] In reactions of this class, vibrationally excited products are formed in the elementary stages of chain propagation. These vibrationally excited species take part in chain branching in different ways. Many complex chemical processes must probably now be analysed with allowance for their energetic non-equilibrium character. The breakdown of the Maxwell–Boltzmann distribution may be brought about not only by a chemical reaction but also by physical methods, for example in plasmochemical and photochemical processes. The production of chemical lasers[10,11] has shown that chemical reactions can be used successfully to convert chemical energy into the energy of coherent optical radiation.

Simple allowance for the reactions of atoms and radicals is insufficient for the kinetic analysis of energetically non-equilibrium processes. It is necessary to know the rate constants of the microscopic processes involving reagents and products in definite quantum states. In this sense it can be said that gas-phase chemical kinetics has now reached the quantum level. Calculations on elementary reactions of this type generally require a detailed analysis of the dynamics of the process, which is not carried out when the transition state method and statistical theory are used.[4-6]

In principle, if quantum effects are insignificant (and this is fairly often the case), the solution of the corresponding problem for a given potential surface is possible using present-day computing methods, even if tens of atoms are involved in the process of chemical rearrangement. As noted above, however, there are practically no data on potential surfaces. Thus the development of theoretical ideas requires

experimental data on the energy distribution in the reaction products, on the intermolecular processes involved in the transfer of different forms of energy, on the intramolecular processes of the transfer of excitation, and on the reactions of species in definite quantum states.

Progress in laser technology has increased sharply the possibilities provided by photochemistry. In laser photochemistry there is extensive discussion of the question of whether selective chemical transformations can be carried out by organising a non-equilibrium state of definite character. An example of selective laser photochemical processes is provided by the separation of isotopes under the influence of laser radiation.[12] The study of the more general principles of selective laser photochemistry is now being carried out in three directions.

1. The selective rupture of molecular bonds in definite positions, and not according to statistical laws. For this it is necessary to develop a method for exciting "local modes" by a powerful short pulse so effectively that they undergo rupture before the energy acquired by the molecule in the pulse is able to undergo statistical redistribution.

2. The carrying out of endothermic reactions at low temperatures by the transfer to the reacting species of that form of energy which is most effective for overcoming the activation barrier.

3. Elementary processes of a new type, which have been called "chemical radiation collisions"[13] are now being discussed. In these new processes, reacting species and photons take part in reactions simultaneously. It should be emphasised that these are not the reactions of reagents excited by light, but reactions in which the powerful electromagnetic field of a light wave changes the potential surface of a system, and hence the probability of the reaction and the reaction channel. The development of studies in this direction is restricted by the need to use very powerful sources of monochromatic radiation.

In the establishment of gas-phase chemical kinetics, most attention has been paid to purely scientific questions, whereas at the present time, fundamental studies are closely related to practical requirements. For example, the study of chemical processes in the atmosphere is related to such practical problems as the preservation of the ozone layer and the purity of the troposphere (smog, acid rain, etc.). The problem of organising economic combustion processes which do not contaminate the environment can now be solved using the details of the chemical mechanism of combustion with allowance for non-equilibrium and hydrodynamic factors. To optimise the operation of the active media in various gas lasers, it is necessary to know the quantitative characteristics of the elementary processes involving the excited species. The search for new active media for chemical lasers is closely related to the study of the energy distribution of reaction products.

Moreover, the organisation of energetically non-equilibrium processes in which the energy is used in the form most effective for overcoming activation barriers may provide a promising route for the development of new processes for chemical technology.

II. METHODS OF LASER SPECTROSCOPY

The present section examines methods for producing and recording labile species (atoms, radicals, excited species). The examination will be restricted to existing methods based on developments in laser technology.

1. Methods of Recording Labile Species

Laser spectroscopy is now widely used for analytical purposes (see the published review[14]). Only those methods which are used in gas-phase chemical kinetics will be examined here.

Laser absorption spectroscopy (LAS). In classical spectroscopy, the absorption method is used successfully, and more frequently than other methods. It is sufficient, for example, to mention the achievements of kinetic spectroscopy combined with flash photolysis.[15] One of the main problems in absorption methods is to increase their sensitivity with a high spectral resolution. Classical light sources generally have insufficient power in a narrow spectral range, and this restricts the sensitivity of classical absorption spectroscopy.

The use of a laser as a light source in the absorption method makes it possible to increase sharply both the sensitivity of the method and the spectral resolution. This is related to the fact that laser radiation is highly monochromatic, directed, and intense. Lasers are now used in both the infrared and visible ranges. Thus a spectrometer has been developed, based on tunable semiconducting lasers, with a working spectral range of 4–20.5 μm and a spectral resolution of $\sim 10^{-3}$ cm^{-1}.[16] Typical parameters of the absorption method (and other methods) are given in Table 1.

Table 1. Comparative characteristics of laser spectroscopic methods.

Parameter	Methods				
	LAS	IRLS	LMR	FP	CARS
Time resolution, s	10^{-6}	10^{-6}	10^{-2}—10^{-3}	10^{-8}—10^{-9}	10^{-8}
Spatial resolution	1 mm	1 mm	1 mm	10^{-6} cm^{-3}	10^{-5}-10^{-6} cm^{-3}
Sensitivity, cm^{-3}	10^{12}—10^{13}	10^{8}—10^{10}	10^{8}—10^{10}	10^{9}—10^{10}	10^{13}—10^{14}
Spectral resolution, cm^{-1}	0.03	0.03	10^{-2}—10^{-4}	10^{-3}	10^{-2}—10^{-3}
Spectral range, μm	0.2—10	0.4—1.2 and 2.7—3.0	4.0—2000	0.2—1.0	infrared range

Laser magnetic resonance (LMR). The physical principles of LMR are similar to those of EPR. The energy of the laser quantum is chosen to be close to the energy gas (ΔE) between two levels of the fine structure in the case of atoms and two rotational or vibrational-rotational levels in the case of radicals. Resonance between ΔE and the energy of the light quantum is achieved using an external magnetic field. The radiation sources used are gas lasers in the sub-millimetre range (H_2O lasers, lasers with optical pumping) and in the infrared range (CO_2 and CO lasers).

The first laser magnetic resonance spectrometer (LMRS) in the sub-millimetre range was developed in the USA in 1970,[17] and the first LMRS operating in the infrared range, based on a CO_2 laser, was developed in 1975 in the Institute of Chemical Physics of the Academy of Sciences of the USSR.[18]

The high sensitivity of magnetic resonance methods is due primarily to the use of magnetic modulation and a synchronous detection system. A second factor increasing the sensitivity is the positioning of the reaction vessel inside the laser resonator. A theoretical analysis of in-resonator absorption in LMR has been carried out,[19] and the theory has been verified

experimentally.[20] It was found that there is an optimum value of the frequency of magnetic modulation (which is close to the frequency corresponding to the characteristic vibrational relaxation of the laser) at which there is a marked increase in the effective length of the optical path. The fact that this optimum frequency is close to the frequency of modulation of standard EPR spectrometers enabled Gershenzon and coworkers[21] to develop a new class of combined EPR–LMR spectrometers, based on standard radio-spectrometers. In this spectrometer, the gas specimen is present simultaneously in the resonator of the EPR spectrometer and in the resonator of the CO_2 laser. The parameters of the LMR method when used under continuous conditions are given in Table 1.

The possible use of LMR with a resolution of ~4 μs was recently demonstrated.[22] The relatively high sensitivity (~10^{11} SiH_3 radicals per cm^3) was achieved by signal accumulation.[22]

In-resonator laser spectroscopy (IRLS). IRLS was proposed by Soviet workers in 1970.[23] The method is based on the influence of the substance being studied on the parameters of laser radiation. In IRLS, the substance being studied, for example a gas with species having narrow absorption lines in the lasing band, is placed in the resonator of a laser with a broad amplification contour. The parameters of the active medium of the laser are selected in such a way that the amplification of the light intensity in it compensates the losses at the mirrors, but does not compensate the losses associated with the absorption being studied (these losses are distinguished by their frequency dependence). The losses at the mirrors correspond to broader bands, compared with the narrow absorption lines of the substance being studied.

The problems related to the analysis of the necessary conditions for obtaining high sensitivity have been described.[24] In IRLS it is possible to use media in which the width of the uniform lasing contour is much greater than the width of the absorption line in gases. It has been shown theoretically and experimentally that the intensity of lasing at the frequency of the absorption line will be described by the equation:

$$I = I_0 \exp\left(-\sigma n \frac{l}{L} ct\right)$$

where n is the concentration of the substance being studied; σ the photon absorption cross-section; c the velocity of light; l the length of the cell; L the length of the resonator; t the lasing time; and I_0 the intensity of the radiation at the start of lasing, which is assumed to be independent of the frequency. The intensity of lasing at other frequencies, not coinciding with the absorption lines, is practically independent of time.

This equation shows that the method is analogous to the absorption method; the optical path length is $(l/L)ct$. For a lasing time of 10^{-3} s and $l/L = 0.3$, the optical path length is 10^5 m. This long optical path length can be achieved with a reaction vessel with small geometric dimensions. At the same time, the brightness of the light source remains high, and it is possible to use spectrographs with a high spectral resolution.

The active media used in IRLS include glasses doped with neodymium, solutions of organic dyes, and alkali metal halide crystals with colour centres.

Laser induced fluorescence (LIF). The LIF method involves the laser excitation of the electronically excited states of atoms and molecules and the subsequent observation of fluorescence from these states. The intensity of the fluorescence in most cases is proportional to the population of the state excited by the light, and this makes it possible to measure the concentration of molecules in this state. The excitation sources used include pulse and continuous lasers, most frequently dye lasers. The fluorescence is usually observed in a direction at right angles to the line of propagation of the laser radiation. The applicability of the method is restricted by the need for a fairly high fluorescence yield. This last requirement, because of the existence of non-radiative deactivation of electronically excited states, restricts the possibilities provided by the method at fairly high pressures. In those cases where the LIF method is applicable, however, it is very effective. This is related to the fact that the method shows high time and spatial resolution and unique sensitivity. The high spatial resolution makes it possible to carry out a local analysis in a very small volume. Theoretically, this volume may amount to λ^3, where λ is the wavelength; in practice, a volume of ~10^3 μm^3 is easily achieved. The time resolution of the method is related to the duration of the pulse (reaching 10^{-12} s).

The highest sensitivity can be achieved using continuous lasers for the excitation; it is often possible to realise saturation conditions, that is conditions in which the species being studied exists for equal times in the excited and ground states. In this case, even a single atom can emit a large number of photons in one second, and this makes it possible to record single atoms.[25] The use of continuous lasers, however, has some disadvantages, such as the relatively small spectral range of operation (400–900 nm) and the low time resolution. For a number of problems, therefore, it is more appropriate to use pulse lasers (particularly in the ultraviolet range) in the LIF method.

The development of non-linear optics has made it possible to move far into the short-wave range of the spectrum using powerful pulse lasers and frequency-doubling crystals. A spectral range to 200 nm is now easily achieved. Lasing at much shorter wavelengths of the spectrum has also been described. For example, the production of non-tunable radiation in the region of 39 nm has been reported.[26]

Active Raman spectroscopy (ARS or CARS). This method is based on the fact that in a field of sufficiently intense light rays with frequencies ω_1 and ω_2 satisfying the condition $\Omega = \omega_1 - \omega_2$ (Ω is the frequency of the molecular vibrations), build-up of molecular vibrations with frequency Ω takes place. As a result, the light ray with frequency ω_1 begins to be scattered on the excited vibrations with the appearance of radiation at the anti-Stokes frequency ($\omega_a = \omega_1 + \Omega = \omega_2 + 2\Omega$). The sensitivity of the method depends on the intensity of the radiation at the frequency ω_a. To obtain sufficiently intense radiation at the frequency ω_a it is necessary that definite relationships between the wave vectors of the light rays with frequencies ω_1 and ω_2 be satisfied. This condition is most frequently satisfied by using collinearly propagating light rays with frequencies of ω_1 and ω_2. Although this configuration is easily realised, it lowers the spatial resolution of the method. There are however methods which make it possible to obtain high sensitivity together with good spatial resolution by this method. CARS has been described in detail.[27] The CARS method most frequently uses the second harmonic of a YAG:Nd^{3+} laser (frequency ω_1) and a tunable laser based on dye solutions (frequency ω_2).

2. Comparison of the Methods

The possibilities of using laser spectroscopy to solve problems in gas-phase chemical kinetics are determined by the following parameters: sensitivity, time resolution (which

characterises the speed of the method), spectral resolution (which makes it possible to record species in definite quantum states), spatial resolution (which shows the possibility of local analysis), and the spectral range of action of the method (which characterises the universality of the method). These characteristics of the methods show that a particular method is preferred for the solution of each problem. The parameters of the methods described above are given in Table 1. It should be emphasised that the figures given in Table 1 are not the best values, but typical values achieved in many studies. The sensitivity depends not only on the method but also on the absorption cross-section of the species being recorded. Since the values of the cross-sections are different for different molecules, the sensitivity of the methods is represented by a fairly wide range of values in Table 1.

Table 1 shows that the absorption method, and also the IRLS and LMR methods, do not make it possible to carry out a local analysis. In those cases where the reaction medium shows symmetry with respect to one of the axes, these methods can be used to analyse the distribution of the concentration of the species in space. A volume local analysis can be carried out only by LIF and ARS methods. These methods also have the highest time resolution. The LIF method has the highest sensitivity, although it is not very general, since the radiative channel for the relaxation of the excitation is often very weak. The ARS method, however, is fairly universal. The use of a tunable laser in this method makes it possible to select any frequency difference $\omega_1 - \omega_2$, so that ARS can be used to record any species in which there is an active Raman transition. A disadvantage of the ARS method is the relatively low sensitivity.

The absorption method and the LMR method are also fairly universal, since they cover the infrared range, in which the vibrational frequencies of many species lie. LMR can record only paramagnetic species, whereas the absorption method can record all species. The sensitivity of the LMR method is much higher, however. The combination of LMR and EPR in a single instrument increases the possibilities provided by LMR, since the measurement of the absolute concentrations by the LMR method can be carried out using EPR, for which a method for measuring absolute concentrations already exists. The LMR method, and also the absorption method using continuous lasers, have relatively low time resolution. Pulse versions of LMR and the absorption method have recently appeared, which make it possible to obtain a time resolution of $\sim 10^{-6}$ s.[16-22] One of the disadvantages of working in the infrared range is the sharp decrease in sensitivity in studies at high pressures, because of pressure broadening of the absorption lines. IRLS makes it possible to work with a high sensitivity at higher pressures. This method also has a fairly high time resolution. IRLS makes it possible to record with a high sensitivity not only absorption, but also the amplification of light when there is inversion of the population of the energy levels in the medium being studied. A disadvantage of the IRLS method is the restriction of the spectral range of applicability in the ultraviolet (to 350 nm).

Comparison of the parameters of the method described shows that the methods supplement one another. The parameters given in Table 1 for these methods show the type of problem for which it is appropriate to use a particular method. Thus ARS should be most widely used to probe flames. In combustion processes, the concentrations of even the labile species are generally relatively high, so that a high sensitivity is not required. For the solution of these problems, primary importance is also acquired by the characteristics of the ARS method, since it is universal, and permits local analysis. For the study of reactions involving radicals, laser spectroscopy in the infrared range is most widely used. It is convenient to use LMR to record radicals. LMR combined with EPR is particularly promising for the study of the kinetics of the reactions between two radicals.

For the study of processes involving very short-lived species, it is appropriate to use pulse methods such as IRLS and LIF, which give the required time resolution. Because of its unique sensitivity, it is also appropriate to use LIF to obtain information on the primary distribution of energy in an elementary chemical experiment.

Specific examples of the use of these methods will be described below.

3. Methods for Producing Labile Species

To study various processes involving labile species, it is necessary to have methods for obtaining them. The present examination will be restricted to laser methods for producing radicals and excited species. The most widely encountered method for obtaining radicals is by flash photolysis. The combination of this method with classical kinetic spectroscopy made it possible to begin the quantitative study of reactions involving radicals. In the classical version of the method, however, it was usually necessary to use a high energy flash to produce the photolysis; the light was not monochromatic. As a result of absorption, part of the light energy was used up in the dissociation of the molecule, and part was liberated in various degrees of freedom of the molecules and their fragments. The existence of excited species of different types and the non-isothermal conditions under which the reaction took place, often made quantitative studies difficult.

The use of the more sensitive methods of laser spectroscopy to record radicals makes it possible to lower considerably the energy of the radiation producing the photolysis. The replacement of the light source by a laser source makes it possible to use monochromatic radiation for the photolysis, and hence to obtain radicals (and other species) with a definite energy content. Another advantage of the use of lasers for the production of radicals and excited species is the possibility of producing the necessary concentration of labile species in a local volume in very short time intervals. If the labile species are recorded in a local volume with very short delay times between the irradiating and probing pulses, even lower irradiation pulse energies are required to produce a detectable concentration of labile species.

The simplest method fairly frequently used to obtain excited species is by direct one-photon optical excitation. This method is most frequently used in the infrared range for the selective excitation of the lower vibrational states of molecules.[28-30] For medium absorption cross-sections $\sigma = 10^{-18}$–10^{-20} cm^2 and existing laser powers, it is fairly easy to achieve saturation conditions, that is to transfer half of the irradiated molecules from the ground to the excited state. An analgous technique can be used to excite the electronic states of molecules in the visible and ultraviolet ranges. The possibilities in this case (from the viewpoint of the ease of obtaining high concentrations of excited species) do not differ greatly from the conditions in the infrared range.

Direct one-photon optical excitation can also be used to obtain excited species in higher vibrational levels. It is possible to use initial excitation of the molecule into an electronically excited state by a quantum of visible or ultraviolet light and subsequent internal conversion of the molecule from the excited electronic state into high vibrational levels of the ground state.[31] Another method involves the direct excitation by a quantum of visible light of the higher overtones of the vibrational transitions of a molecule. In spite of the fact that the cross-section of this process is small, the high power of the laser source makes it possible in a number of cases to

produce an appreciable concentration of molecules in states excited to high vibrational levels.[32,33]

The high power of laser radiation makes it possible to use multiphoton processes of different types to produce excited species. These processes include, for example, Raman scattering, in particular stimulated Raman scattering (SRS). In a number of cases it is possible to obtain up to 10^{16} photons at the Stokes frequency after one laser pulse. Since each photon at the Stokes frequency corresponds to one excited molecule, it can readily be seen that SRS can be used to obtain appreciable concentrations of excited species. It is particularly fortunate that when Raman scattering is used, it is possible to excite the levels of molecules corresponding to transitions which are inactive in the infrared spectrum and which therefore cannot be excited by direct optical excitation, for example the totally symmetric vibration (in particular, it is possible to excite the homonuclear diatomic molecules H_2, N_2, etc.).

Excited species are often produced by SRS under pre-threshold conditions at low pressures of the mixture being studied. Laser radiation with two frequencies in the visible range ω_1 and ω_2 is directed on to the object being studied, and the frequency difference corresponds to the frequency of the vibrational transition of the molecule being studied. The radiation of frequency ω_1 is usually the powerful radiation of a non-tunable laser (for example the second harmonic of a YAG : Nd^{3+} laser), and the radiation of frequency ω_2 is obtained by SRS in a high-pressure cell filled with the substance being studied. The use as the source of the radiation ω_2 of the frequency-tunable radiation of a dye laser (two-frequency coherent excitation (TCE) method[34] is promising. The multiphoton infrared excitation of molecules has been widely used.[35,36]

Methods for obtaining species excited to definite levels of internal degrees of freedom have not yet been considered. In a number of cases, however, laser methods also make it possible to obtain molecules with a velocity vector of definite magnitude and direction. If a molecule for which the line contour is determined by Doppler broadening is excited using a laser whose spectral width is appreciably smaller than the width of the absorption line, then only molecules moving at a definite velocity in the direction of the laser beam will be excited. For example, if the laser frequency corresponds to the frequency of the centre of the absorption line, only the molecules "at rest" will be excited.[37] Laser methods also make it possible to excite orientated molecules in definite fashion. Use is made of the polarisation of the laser beam, that is the fact that when radiation interacts with matter, selective excitation is undergone by those molecules for which the transition moment is parallel to the light polarisation vector. It is thus possible to study the reactions of molecules oriented in definite fashion and to investigate the influence of steric factors on the course of a reaction. Some examples will be given later.

III. THE USE OF LASERS IN GAS-PHASE CHEMICAL KINETICS

In this section, an attempt will be made, using specific examples, to demonstrate the possibilities provided by the use of lasers to solve problems in gas-phase chemical kinetics.

1. Elementary Reactions Involving Radicals

The modern development of the theory of chemical transformations, and the increasing demands being made by the chemical industry, require increasingly reliable and accurate quantitative data on the rate constants of elementary reactions. In addition, an important field of study has appeared, namely the chemistry of the atmosphere, in which traditional macro-kinetic methods are probably generally inapplicable, and the modelling of chemical processes by a set of elementary reactions is of decisive importance. Most gas-phase reactions involve the participation of atoms and radicals. The greatest experimental difficulties are encountered when recording polyatomic radicals. Table 2 gives examples of elementary processes of several types involving polyatomic radicals: a) reactions of radicals with stable molecules; b) reactions between radicals; c) processes involving the heterogeneous destruction of radicals. The examination has been restricted to several examples of reactions involving radicals consisting of three or more atoms.

Table 2. Some elementary reactions of radicals, studied by laser spectroscopy.

Radical	Reagent	Method
NH_2	NO [38—40]; O_2 [41, 42]; O_3 [43, 44]; C_2H_4, C_2H_2 [40]; HO_2; NH_2 [45]; CH_3 [46]	IRLS [38, 42, 43, 45]; LAS [41]; LIF [39, 40, 44, 46]
CHF	O_2, NO [47]	LIF [47]
HCO	O_2 [48, 49]; NO [48, 50]; H [51]; HCO [52]	IRLS [48-52]
HNO	NO, HNO [53]	IRLS [53]
PH_2	O_2 [54], PH_2 [55]	IRLS [54, 55]
HO_2	NO [56]; HO_2, O, Cl, OH [57,58]; ClO[59]; H[60]	LMR [56-60]
NF_2	NF_2 [61]; O, N, F, H [62]	LMR [61, 62]
CH_3O	O [63]	LIF [63]
$C_6H_5CH_2$	O_2, Cl_2 [64]	LIF [64]
NH_2	surface of quartz reaction vessel	IRLS [38]; LIF [40]
HO_2	ditto	LMR [65]

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

The high reactivity of radicals makes it difficult to obtain them in sufficiently high concentrations. Moreover, if it is nevertheless possible to create high concentrations of radicals, the study of the reaction of a radical with a molecule is always made difficult by the existence of quadratic reactions involving the interaction between radicals. Thus one of the basic features required of modern methods for studying elementary reactions is a high sensitivity. It can be seen from Table 2 that it is because of the low sensitivity of the CARS method that it is not usually employed for the quantitative study of elementary reactions. All the other methods discussed earlier are used to study elementary reactions.

An attempt will now be made to discuss the advantages and disadvantages of each method in relation to the problem being discussed in the present section. LMR is attractive primarily because of its universality and the possibility of recording (particularly for LMR using lasers in the sub-millimetre region of the spectrum) many paramagnetic species involved in an elementary reaction. In addition, the possibility of obtaining the EPR and LMR spectra simultaneously using combined LMR–EPR spectrometers facilitates the task of determining absolute concentrations in the study of the reactions of radicals, when the concentrations of the reacting species are comparable.

In a study[62] of the reaction $O + NF_2$ using a combined LMR–EPR spectrometer, [O], [NF_2], and [F] were recorded. This made it possible to obtain the rate constant of this reaction and to determine the main channel by which it takes place

$$O + NF_2 \rightarrow FNO + F$$

The following reversible reaction has been studied:[56]

$$HO_2 + NO \rightleftarrows OH + NO_2$$

This work[56] is of interest from the methodological viewpoint, since the concentrations of the species OH, HO_2, and NO_2 were measured. This made it possible to study the temperature dependence of the rates of both the forward and back reactions.

A disadvantage of the LMR method is its low time resolution. For this reason, LMR is combined with flow methods. When sufficiently rapid gas streams are used, the effective time resolution can be brought to $\sim 10^{-3}$ s. Nevertheless, in the study of a reaction under flow conditions, side processes of different kinds, for example heterogeneous processes, may be superimposed on the reaction being studied. It was noted above than an LMR method with a high time resolution has been developed.[22]

The IRLS and LIF methods have a fairly high time resolution (see Table 1). They can therefore be used in static systems with the flash production of radicals. The use of these methods, because of their high time resolution, makes it possible to avoid the influence of heterogeneous processes, that is to study a reaction in a time which is shorter than the diffusion time of the active species to the walls of the reaction vessel. An example is provided by the use of IRLS to study the reactions of PH_2 radicals.[54,55] Another important advantage of IRLS in the visible wavelength range is that it can be used at high pressures in the system. This makes it possible, for example, to measure the rate constants of fairly slow reactions. IRLS, combined with flash photolysis, has been used[42] to study the destruction of NH_2 radicals, formed by the photolysis of NH_3, in the presence of O_2. The total pressure in the system reached 570 mmHg, and in principle could have been even higher. This made it possible to estimate the rate constant of the reaction $NH_2 + O_2 \xrightarrow{k_1}$ products; $k_1 < 3 \times 10^{-18}$ $cm^3\ s^{-1}$. IRLS has also been used[66] to estimate the rate constant of an even slower reaction: $HNO + O_2 \xrightarrow{k_2}$ products; $k_2 < 8 \times 10^{-20}$ $cm^3\ s^{-1}$.

The main disadvantage of the IRLS method is its as yet short spectral range of action, which restricts the universality of the method. At the same time, the use of radiation in the infrared range within the framework of this method is now being developed, and this should extend considerably the possibilities provided by the method.

The data in Table 1 show that the LIF method has the highest limiting sensitivity. Although as already noted the requirement of a high fluorescence quantum yield restricts the number of species which can be followed by this method, it is widely used, particularly in other countries, to study the kinetics of chemical reactions. The method has been used to measure the rate constants of a large number of reactions involving both diatomic (OH, SH, CH, C_2, etc.)[67,68] and polyatomic (NH_2, CHF, CH_3O, $C_6H_5CH_2$, etc.) radicals. Some examples of reactions involving polyatomic radicals, which have been studied by LIF are given in Table 2.

LIF based on continuous dye lasers is fairly frequently used to measure reaction rate constants. As in the case of LMR, a flow system is used. An example of studies of this kind is provided by the measurement[40] of the rate constants of the reactions of the NH_2 radical with NO, NO_2, C_2H_2, C_2H_4, allene, etc.

The most promising development from the present viewpoint is the combination of LIF with laser flash photolysis. Thus the reaction $OH + C_2H_4$ has been studied in the temperature range 291–591 K at pressures of 50–600 mmHg.[69] The OH concentration was followed by LIF using a quasi-continuous dye laser, which produced a sequence of lasing pulses with a duration of 8–10 picoseconds and a repeat frequency of 246 MHz. This made it possible to study the kinetics of the destruction of the OH radicals formed in the photolysis of an $N_2O + H_2O$ mixture under the influence of the radiation from an excimer laser based on ArF. The initial OH concentrations measured immediately after the photolysing pulse were 5×10^9–10^{11} cm^{-3}. In this study,[69] LIF was used up to a pressure of 600 mmHg. This was made possible by the sensitivity reserve of the method, in spite of the appreciable quenching of the fluorescence of the radicals at this pressure. LIF has been used[70] to study the reaction† $OH + NO_2 + M \rightarrow HNO_3 + M$ at pressures up to 10 atm.

2. Elementary Processes Involving Excited Species

Elementary processes involving excited species are molecular collisions accompanied either by a change in the energy of the internal degrees of freedom of the colliding species or by chemical transformations. The study of the reactions of species in definite quantum states is closely related to the study of the energy distribution of the products of the elementary reactions. This relationship exists as a consequence of the principle of microscopic reversibility. The present section therefore examines three types of elementary process: a) processes involving the transfer and relaxation of the energy of the internal degrees of freedom in the collisions; b) the reactions of the excited species; and c) the energy distribution of the products of the elementary reactions.

Studies of these processes can make an important contribution to the development of ideas which make it possible to understand the type of reactions in which a particular form of energy is most effective for overcoming the activation barrier. At the same time, the existence of these ideas will probably make it possible to formulate more general regular features for complex energetically non-equilibrium chemical reactions. The study of the reactions of excited species will help in the investigation of the dynamics of the interaction of the species. The rate constants of elementary reactions obtained under Maxwell–Boltzmann distribution conditions in fact carry little information on the dynamics of the interaction of the species. The specification of definite quantum states of the reagents and products makes it possible to detect finer details of the dynamics of collisions and the influence of the characteristics of the potential energy surfaces on the dynamics.

Information on the energy distribution of the reaction products is particularly important. These data make it possible to resolve the question of the possibility of using these reactions as active media for transforming chemical energy into coherent radiant energy. In addition, quantitative data on the behaviour of excited species are necessary for an understanding of specific energetically non-equilibrium processes taking place in chemical lasers, plasmochemical reactors, the upper layers of the atmosphere, etc.

a) Processes involved in the transfer and relaxation of the energy of internal degrees of freedom in collisions

These processes are now being fairly widely studied in both physical and chemical laboratories. The experimental results and theoretical analyses of these processes have been given in detailed monographs.[71,72]

These processes will therefore be dealt with very briefly; the treatment will be restricted to a few types, to demonstrate the possibilities provided by laser technology. Table 3 gives examples of various processes of this kind, with an indication of the methods used to produce and record the excited species.

The first example in Table 3 demonstrates the possibilities provided by laser methods for both the production and recording of excited species. The TCE method used to

†Here, M represents an inert-gas molecule.

produce excited species is very promising. In particular, this method makes it possible to obtain appreciable concentrations of excited species not only in lower but also in higher vibrational excited states. The second example demonstrates the possibility of studying processes of vibrational–vibrational (v–v) exchange for isotopic molecules. LAS, because of its high spectral resolution, makes it possible to record both isotopic species. The last example shows that the processes involved in the transfer and relaxation of vibrational energy are now being studied not only for stable species, but also for radicals.

Table 3. Examples of processes of vibrational relaxation and energy redistribution studied by laser spectroscopy.

No.	Process	Method of excitation	Method of recording	Refs.
1	$CO_2(10^00)+CO_2(01^10) \rightarrow CO_2(11_10)+CO_2(00^00)$	TCE	CARS	[75]
2	$^{12}CH_3F(\nu_3)+{}^{13}CH_3F(0) \rightarrow {}^{12}CH_3F(0)+{}^{13}CH_3F(\nu_3)$	CO_2 laser	LAS	[74]
3	$NH_2(010)+M \rightarrow NH_2(000)+M^{**}$	FP*	IRLS	[75, 76]

*Flash photolysis.
**Here, M represents a molecule of He, Ar, CO, N_2, NH_3, O_2, or C_2H_4.

b) Reactions involving excited species

A large number of studies of reactions involving vibrationally or electronically excited species have now been carried out. The possibilities provided by the use of lasers in this field are illustrated by reactions of three types: the reactions of excited molecules with atoms, the reactions of excited molecules with stable molecules, and reactions involving the isomerisation and decomposition of excited molecules (Table 4).

Table 4. Examples of chemical reactions involving excited species.

No.	Reaction	Method of excitation	Refs.
1	$O+O_3(v) \rightarrow 2O_2$	CO_2 laser	[28]
2	$Br+CH_2F(v) \rightarrow HBr+CH_2F$	CO_2 laser	[29]
3	$Sr+HF(v) \rightarrow SrF+H$	HF laser	[30,77]
4	$NO_2^*+NO_2 \rightarrow 2NO+O_2$	Ar laser	[78,79]
5	$NO_2^*+CO \rightarrow CO_2+NO$	Dye laser	[80]
6	$NO_2^*+C_2F_4 \rightarrow CF_2O+CF_2+NO$	ditto	[79]
7	$O_3(v)+NO \rightarrow NO_2+O_2$	CO_2 laser	[81]
8	$O_3+NO(v) \rightarrow NO_2+O_2$	CO laser	[81]
9	$H_2C{=}CHCH_2NC+h\nu \rightarrow H_2C{=}CHCH_2CN$	Dye laser	[82]

*NO_2^* denotes an electronically excited NO_2 molecule.

Reaction No.1 was studied in Ref.28. The O_3 molecules were first excited by the radiation from a CO_2 laser (direct one-photon optical excitation (DOOE) into the first vibrational level of the vibrational modes ν_2 (or ν_1) and ν_3. The efficiency of the vibrational energy in overcoming the activation barrier of this exothermic reaction was determined.

Reaction No.2 was studied in Ref.29. DOOE was again used to produce the vibrationally excited species. The experiments showed that under the influence of the radiation of a CO_2 laser with a power of 20 W, the reaction rate increases by factors of several tens or hundreds (the increase is particularly marked at low temperatures). This increase in rate cannot be attributed to the participation in the reaction of only those vibrationally excited states of CH_2F which are excited directly by the laser radiation. This led the authors[29] to suggest that the increase in the rate of reaction is due to the participation in it of higher vibrationally excited states formed in processes of v–v exchange of energy. The authors showed that the vibrational energy is effective in overcoming the activation barrier of this reaction.

The study of the reactions of Sr atoms with the HF molecule in states with $v = 0$ or 1 (reaction No.3 in Table 4) is of considerable interest.[30,77] The reactivity of vibrationally excited HF molecules ($v = 1$) was studied using the so-called beam–gas configuration, that is the beam of Sr atoms from the furnace was directed into a cell containing hydrogen fluoride at a low pressure (~10^{-4} mmHg). The HF molecules were excited into the state with $v = 1$ by DOOE using an HF laser. The kinetics of the reaction were followed by LIF, by recording the reaction product SrF. It was found that the cross-section of this endothermic reaction ($\Delta H = 6.4 \pm 1.6$ kcal mole^{-1}) for HF ($v = 1$) is greater by at least four orders of magnitude than that for HF ($v = 0$).

The authors cited[30] compared their data with the results of a study of the dependence of the cross-section of reaction No.3 on the translational energy of the HF molecules. In this case, crossed molecular beams of Sr and HF were used. The reaction was again followed by LIF, from the product SrF. Comparison of the results of the two experiments showed that vibrational energy is apparently slightly more effective than translational energy in overcoming the activation barrier of the reaction.

Examples of the reaction of excited species with stable molecules are provided by the reactions of excited NO_2^* molecules with NO_2, CO, and C_2F_4.[78–80] In these studies, the NO_2 molecules were excited either by an argon laser or by dye lasers. The reaction $NO_2 + NO_2 \rightarrow 2NO + O_2$ is endothermic, whereas the reaction $NO_2 + CO \rightarrow CO_2 + NO$ is exothermic. Nevertheless, the rate constants of the reactions of the excited molecules NO_2^* with NO_2 and CO show the same dependence on the wavelength of the irradiating light. This fact is difficult to explain if it is assumed that only the vibrational form of the energy is effective in overcoming the activation barrier in these reactions.[79]

Table 4 also gives examples of processes involving the isomerisation of a molecule under the influence of laser radiation. The direction and rate of these reactions depend significantly on processes of intramolecular energy redistribution.

In a polyatomic molecule, even in the absence of collisions, as a result of the strong interaction of different degrees of freedom in a short time, relaxation processes take place, which wipe clean from the "memory" of the molecule those states in which it existed immediately after excitation, and these lead finally to some statistical distribution of the energy in the molecule. This raises the interesting question of whether it is possible to achieve conditions in which a chemical reaction is able to take place before the complete statistical redistribution of the energy. In this case it might be possible to control the directions of reactions by means of laser radiation. Thus one of the principal tasks in laser chemistry involves the investigation of the possibility of carrying out chemical reactions not according to statistical laws under the influence of a laser.

Until recently it was generally accepted that the processes involving the intramolecular redistribution of energy for polyatomic molecules at a sufficiently high level of excitation take place very rapidly (in times $\lesssim 10^{-12}$ s). This assumption was based, for example, on a large amount of experimental data on chemical activation, which are effectively explained by RRKM theory for unimolecular reactions. According to this theory, the energy of vibrational excitation of a molecule is able to undergo complete redistribution within the complex molecule, in times shorter than the characteristic time of the reaction, so that the decomposition obeys the laws of statistics. It has been suggested,[83,84] however, that in some cases the statistical theory (RRKM) effectively explains experiments on chemical activation because of the statistical character of the formation of the excited molecules.

A number of successful attempts have now been made to follow intramolecular processes of energy redistribution. These studies can be divided into two groups. The first group consists of studies of spectra containing bands which are assigned to the high overtones of the vibrations of polyatomic molecules. Highly sensitive methods of laser spectroscopy, IRLS and optico-acoustic spectroscopy, have made it possible to record the spectra of the overtones of the vibrations of a large number of molecules.[85,86] The width of the lines in these spectra is related to the lifetime of the excited state by the uncertainty relation. The recorded spectra generally relate to the overtones of the strongly anharmonic vibrations of C–H and N–H bonds. In most cases, the line width is large (for example 100 cm^{-1} for benzene[85]). This corresponds to lifetimes of the state of ~10^{-13} s. On the other hand, in a number of cases it is possible to observe the spectra of the high overtones of molecules with fairly narrow lines (for example, for NH_3 and C_2H_2 the line width is 0.3 cm^{-1} for excitation energies of ~2 eV).[86] This should apparently indicate a low rate of energy redistribution in this case. The second direction of studies involves the measurement of the rates of different unimolecular reactions of molecules which have been vibrationally excited as a result of the absorption of one quantum of laser radiation, and the comparison of the reaction rate constant obtained[33,82] with RRKM theory.

Table 5.

Reaction	Method of recording	References
$Ca(^1P_1) + HCl \rightarrow CaCl(A^2\Pi) + H$	LIF	[87]
$Ca(^1P_1) + HCl \rightarrow CaCl(B^2\Sigma) + H$	LIF	[87]
$O(^1D) + RH \rightarrow R + OH$	LIF	[88]
$HONO + h\nu \rightarrow OH + NO$	LIF	[37]

The unimolecular isomerisation of allyl isocyanate $H_2C{=}CH{-}CH_2NC$ has been studied.[82] The levels excited corresponded to the overtones of the vibrations of different C–H bonds in the molecule: saturated–alkene ($H_2C{=}$), unsaturated–alkene ($=CH-$), and methylene ($-CH_2-$). The excitation was carried out by placing the substance being studied in the resonator of a dye laser tuned to the wavelength corresponding to the absorption of the overtone being studied. The course of the reaction was followed by measuring the concentration of the reagents by an optico-acoustic method.

It was concluded[82] that the measured rate of isomerisation is slightly greater than that predicted by RRKM theory. Moreover, the reaction rate was found to depend markedly on the type of vibration excited (the highest rate was observed for the excitation of the vibrations of the $=CH-$ group). The results apparently indicate that on laser excitation, the allyl isocyanate molecule undergoes isomerisation more rapidly than the complete statistical redistribution of the energy within the molecule. It should be noted that although the observed deviations from RRKM theory are fairly small, their smallness, as pointed out by the authors cited,[82] may be related to different relaxational collision processes which "mask" the significant role of non-randomised states in the reaction.

c) The energy distribution of the products of elementary reactions

Examples of studies of this type are given in Table 5. As already noted, in the study of reaction No.3 (Table 4) by LIF, the molecules of the product SrF, formed in different quantum states, were recorded. The dependence of the distribution of the SrF molecules with respect to vibrational states on the direction of the polarisation of the radiation of the HF laser exciting the molecule of the HF reagent into the first vibrational level was observed. Thus when the polarisation of the laser beam was perpendicular to the direction of the beam of Sr atoms, the observed distribution of SrF molecules with respect to vibrational degrees of freedom for the reaction Sr + HF ($v = 1$, $J = 1$) corresponded to the following relationship: $v_0 : v_1 : v_2 = 1.00 : 0.63 : 0.29$. If however the polarisation of the laser beam was parallel to the direction of the beam of Sr atoms, the observed distribution was different: $v_0 : v_1 : v_2 = 1.00 : 0.72 : 0.13$. This experimental result agrees with theoretical predictions based on the assumption that the minimum in the reaction path for the reaction of HF with alkaline earth metal atoms corresponds to a bent configuration of the molecule.

It has also been shown[37,88] that laser methods can be used to study the influence of the relative orientation of the molecules of reagents on the energy distribution of the products. The reaction of Ca ($^1P_1$) atoms with the HCl molecule was studied.[88] The Ca atoms were excited into the state $^1P_1$ from the ground state $^1S_0$ using a dye laser with a wavelength of 422.6 nm. The atom beam–gas configuration (pressure ~10^{-4} mmHg) was used. The fluorescence of the CaCl molecules in the states $A^2\Pi$ and $B^2\Sigma$ formed in the course of the reaction was observed. It was found that when the polarisation of the exciting laser beam changed from the parallel (relative to the direction of the beam of Ca atoms) to the perpendicular, the intensity of the fluorescence from the state $B^2\Sigma$ decreased by 16%, and the fluorescence from the state $A^2\Pi$ increased by 7%. Since there were a large number of factors decreasing the selectivity of excitation, the authors cited pointed out that the significant influence of the geometry of the approach on the ratio of the channels by which the reaction takes place is being observed.

There have been a large number of studies of the distribution of the rotational and vibrational energy of OH radicals formed by the reactions of a $O(^1D)$ atom with different hydrogen-containing molecules. Thus the dynamics of the reaction of the $O(^1D)$ atom with saturated hydrocarbons has been studied.[89] Oxygen atoms in the singlet excited state $O(^1D)$ were obtained by the laser photolysis of ozone: $O_3 + h\nu \rightarrow O(^1D) + O_2(^1\Delta)$ using the radiation of the fourth harmonic of a YAG:Nd^{3+} laser (duration 7 ns). With a short (20 ns–0.5 μs) delay after the photolysing pulse, the energy distribution of the OH radical reaction product was probed by LIF (a dye laser with a pulse duration of ~10 ns was used).

The distribution of the energy in OH radicals, formed in the course of the reaction, among the vibrational and rotational degrees of freedom was measured. The data on the distribution of the rotational energy are of considerable interest. It was found that the distribution is "bimodal" in character, indicating the existence of two reaction channels. One channel corresponds to a rotational distribution in which only the levels with small quantum numbers J are extensively populated. This channel was interpreted as the direct abstraction of an H atom from the hydrocarbon. The second channel corresponds to a broad distribution, in which levels with high values of J are also extensively populated. The second reaction channel was interpreted by the authors cited as the insertion of an O atom into the hydrocarbon molecule with the formation of an excited alcohol molecule, and its subsequent decomposition. The high value of the surprisal parameter indicates that the decomposition of the alcohol molecule is non-statistical in character. The channel involving the abstraction of an H atom is more characteristic of the higher hydrocarbons C_3H_8 and $C(CH_3)_4$, whereas for CH_4 and C_2H_6 a large contribution is made by the reaction channel involving the formation of the excited alcohol molecule.

Important information on the dynamics of the elementary act can be obtained by using laser methods to study photodissociation processes. In this case, the decomposition of a molecule excited by light is often described as "a half collision", signifying that the study of the decomposition of the excited molecule as it were gives half of the information on the inelastic collision of molecules, which takes place via the formation of the same excited state as the photodissociation.

Laser methods have been used[37] to study the photodissociation of the molecule of *trans*-nitrous acid (HONO). The *trans*-HONO molecule was excited by laser radiation with a wavelength of 369 nm, and it decomposed rapidly to OH and NO. The HONO molecule decomposes so rapidly that the molecule is unable to undergo a significant change in its orientation in the time interval between the absorption of the light quantum and its decomposition. The distribution of the energy of the OH radical reaction product among the different degrees of freedom was studied by LIF. It was found that the Doppler contour of the LIF excitation lines of the OH radical has a split maximum, corresponding to a small fraction of OH molecules having their velocity vector directed at right angles to the direction of the laser beams. Because of the polarisation of the radiation of the photolysing laser, only the molecules orientated in such a way that the dipole moment of the transition was parallel to the direction of the polarisation were excited, so that it can be stated that the OH radicals formed in the photodissociation of HONO move apart chiefly in a plane perpendicular to the transition moment of the HONO molecule. Modelling of the line contour form of the fluorescence excitation spectrum showed that the average rate of divergence of the OH radicals was ~2.58 km s^{-1} (which corresponds to a translational energy of 4720 cm^{-1}). From momentum conservation considerations it was found that the translational degrees of freedom of the OH and NO fragments correspond to 72% of the energy liberated in the photodissociation. The distribution of the OH radicals with respect to the rotational degrees of freedom was studied for different directions of the polarisation of the radiation of the photolysing laser. This established that the axis of rotation of the OH radicals is oriented preferentially in a direction parallel to the transition moment of the HONO molecule. It was established that the effective rotational temperature of the OH radicals is close to room temperature, and that there exists a state of non-equilibrium between the levels of types F_1'' and F_2'' (components of spin–orbit splitting).

The above studies show that extensive and detailed information on the dynamics of the elementary act can be obtained by laser methods.

3. Diagnostics of Complex Chemical Reactions

Until recently, because of the lack of sensitive methods for recording radicals, conclusions about the mechanisms of complex chemical reactions were reached on the basis of macrokinetic measurements of the concentrations of the original reagents and the stable products. The appearance of direct methods for studying elementary reactions has made it possible to confirm conclusions about the mechanism of a complex reaction by experimental data on key elementary stages. This method of investigating a complex mechanism remains basic today. This is because even the methods of laser spectroscopy usually do not have sufficient sensitivity for the diagnostics of slow chemical reactions. For chain branched reactions, however, the diagnostics of unstable intermediate species can be successfully undertaken by the methods described above. Thus LMR has recorded the SiH_3 radical in a rarefield flame of $SiH_4 + O_2$ [89] or $SiH_4 + Cl_2$,[90] and also the HO_2 radical in a rarefied $H_2 + O_2$ flame.[91]

A more general approach to the investigation of the mechanisms of chain branched reactions is possible by carrying them out under conditions of stationary isothermal propagation of the reaction zone.[92–94] The macrokinetic characteristics in this case are given by the measured dependence of the rate of propagation of the reaction zone on the initial conditions. Concentrations of intermediate species sufficient for recording by the methods of laser spectroscopy are formed in the reaction zone. Combined measurements of the concentration profiles of the intermediate species and the rate of propagation of the reaction zone would probably make it possible, in a comparatively small number of experiments, to obtain sufficient information to establish reliably the reaction mechanism.

The possibilities provided by kinetic laser spectroscopy in the study of elementary reactions are leading to the development of another approach to the establishment of the mechanisms of complex chemical reactions. The essential feature of this approach is the "construction" of the mechanism of a complex reaction on the basis of a systematic study of the elementary reactions, after which it is tested to find out whether it can explain available data obtained by macrokinetic measurements. This approach has been used[66] to investigate the mechanism of the photo-oxidation of ammonia. This approach is generally very laborious, however.

Even greater difficulties arise in the description of combustion processes. In this case the complex reaction mechanism is influenced by the non-isothermal course of the process and by hydrodynamic factors. It is for this reason that the study of combustion processes requires laser methods which have a high spatial resolution. The CARS and LIF methods are preferred in the diagnostics of combustion processes.

The possibilities provided by the use of these methods to study combustion processes have been reviewed.[95] It may be noted that certain difficulties are also encountered when both CARS and LIF methods are used in the diagnostics of combustion. In the first place, difficulties in the application of these methods are introduced by a whole range of effects of stray light: the luminescence of the flame, the scattering of the laser beam on non-uniformities, the luminescence of aerosol particles under the influence of the laser beam, etc. These phenomena introduce particular difficulties in the application of the LIF method. Another difficulty associated with

its use is the quenching of the fluorescence. Although the high sensitivity of LIF combined with the fairly high concentration of the species also makes it possible to observe fluorescence which has been partly quenched (even by many orders of magnitude of the intensity), the indeterminate nature of the rates of quenching and their possible dependence on the concentrations of various substances in the flame make it difficult to obtain a reliable profile even for the relative concentration of the species being studied in the flame. At the present time, however, the so-called saturated LIF method [96,97] has been developed, in which the study of the dependence of the signal of partly saturated LIF on the power of the exciting laser makes it possible to determine the rate of quenching of the fluorescence and the relative concentration of the material being studied in a given local volume.

The absence of fluorescence quenching, the high universality, and the weaker influence of stray scattering of various kinds (since the observation is carried out in the anti-Stokes region of the spectrum) make the CARS method very convenient for the study of combustion processes. A disadvantage of the method is the existence of a non-resonance scattering signal, which restricts the possibilities provided by the measurement of the concentrations of those species which make up a small fraction of the main gas; at the same time, the improvement of the CARS method suggests that this difficulty will be overcome. [98]

Although absorption methods do not make it possible to measure local concentrations at a given point, they can be used in the study of so-called planar flames. In this case the spatial resolution may be fairly high. Here, it is appropriate to mention the possibilities provided by the use of IRLS, particularly in the version where Raman scattering is used. [99] In this case, in addition to the universality of the IRLS method, there is also the advantage that it is only weakly sensitive to losses which are weakly dependent on frequency, and is not sensitive to stray scattering.

In a large number of recent studies, laser methods have been used to investigate combustion processes. Only some of these will be mentioned. LIF has been used [100] to measure the OH and NH concentration profiles in a stoichiometric $CH_4 + N_2O$ flame. It was also possible to obtain the temperature profiles in this flame. LIF, LAS, and analysis of the products have been used [101] to study the formation of polycyclic aromatic hydrocarbons in rich $CH_4 + O_2$ flames.

The CARS method and other methods using Raman scattering induced by laser radiation are also widely employed in the study of flames. The use of CARS to measure the concentrations of N_2, O_2, H_2, H_2O, CO, CO_2, and CH_4 in a flame has been reported. [95] CARS has also been used to measure the temperature profiles in engines. [102]

4. Laser Chemical Technology

The demands being made of chemical technology are constantly increasing, due largely to various aspects of environmental protection. The question of the creation of a chemical technology without waste is now being considered. Selective laser photochemistry opens up promising routes for achieving this in certain cases. The possibilities provided by the use of laser photochemistry in chemical technology have been reviewed. [103–105]

This question can be examined briefly by considering several examples of selective laser-chemical reactions, given below:

Reaction	Method of excitation	References
$N_2 + O_2 + h\nu \rightarrow 2NO$	SRS	[106]
$2NO_2 + C_2F_4 \xrightarrow{h\nu} CF_2O + 2NO$	argon laser	[79]
$C_2H_4Cl_2 \xrightarrow{h\nu} C_2H_3Cl + HCl$	excimer laser	[107]

The binding of atmospheric nitrogen is an endothermic reaction. It represents the first example of a reaction involving vibrationally excited molecules obtained by laser methods. In Ref. 106, vibrationally excited nitrogen molecules were obtained by stimulated Raman scattering.

The oxidation of tetrafluoroethylene by nitrogen dioxide is an example of an exothermic reaction having an activation barrier. Thus at room temperature the dark reaction $NO_2 + C_2F_4$ takes place very slowly and non-selectively to give several products – fluorophosgene, tetrafluoroethylene oxide, perfluoroacetaldehyde, etc. When the isothermal (at 300 K) reaction is carried out under the influence of an argon laser, its rate increases by a factor of several tens, and the reaction takes place selectively to give the single product fluorophosgene. [79] It is possible to carry out this reaction selectively in another direction to give a product of practical importance, namely tetrafluoroethylene oxide. An unsatisfactory feature of this process is the fairly low quantum yield.

The third example is of interest in that laser radiation is used to bring about a chain reaction; in this case, therefore, the quantum yield of the product is very high ($\sim 10^3$). Laser photolysis only brings about chain initiation, and this makes it possible to carry out the reaction at lower temperatures than in thermal initiation. This leads to a decrease in the yield of side products, that is to an increase in the selectivity of the reaction. The advantage of the laser as photolysing source is that it is possible to achieve a high intensity of the monochromatic light which influences only the starting material, and does not bring about photolysis of the products.

Another promising application of lasers in chemical technology is the laser purification of materials. [108] The principles of laser purification are based on the selective action of the laser radiation on the impurities. The essential features of the method reduce to the conversion of the impurity molecules under the influence of radiation into species which can be readily removed from the reaction vessel. The photolysis of the impurities is carried out either by multiphoton dissociation under the influence of lasers in the infrared range or by one-photon dissociation using lasers in the visible or ultraviolet ranges. An example of the use of lasers in the infrared range is provided by a study [109] involving the selective multiphoton dissociation of organic impurities in $AsCl_3$ under the influence of a pulse CO_2 laser.

It should be noted that when multiphoton dissociation is used to purify gases, a larger proportion of the light energy of the laser is used up in heating the main material. In addition, the selectivity of action may be lowered as a result of collision processes at higher gas pressures. It may therefore be assumed that the use of lasers in the visible and ultraviolet ranges should be more promising for the laser purification of gases. The example of the use of an excimer laser to purify synthesis gas (a mixture of CO and H_2) from hydrogen sulphide can be considered. It is well known that, using catalysts, valuable materials can be obtained from synthesis gas; even extremely small quantities of H_2S impurity, however, poison the catalyst. It has been shown [110] that laser purification makes it possible to lower the concentration of sulphur-containing compounds in synthesis gas to below 10^{-7}, which is sufficient for effective operation of the catalyst. The authors cited [110] also carried out preliminary estimates of the economics of laser purification of the gas. They concluded that for an H_2S concentration below 10^{-6}, the use of excimer lasers to purify synthesis gas is economically favourable.

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Phospha-alkynes—Compounds of Monocoordinate Phosphorus

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The review gives a systematic account of and surveys the results of studies on compounds of monocoordinate phosphorus. The methods of synthesis of phospha-alkynes from phosphines and phospha-alkenes (by pyrolysis or low-temperature elimination), their structure and physico-chemical properties, and also their chemical behaviour in complex-formation and cycloaddition reactions are examined.
The bibliography includes 52 references.

CONTENTS

I. Introduction 243
II. Synthesis 243
III. Structure and physicochemical properties 245
IV. Chemical properties 246

I. INTRODUCTION

The synthesis of phosphaethyne (H−C≡P) in 1961[1] laid the foundation of the class of organophosphorus compounds (OPC) which are derivatives of monocoordinate phosphorus (phospha-alkynes). The first communication about the synthesis of a compound of this type (NaCP) dates back to 1894,[2] but subsequent attempts to reproduce the experiments described in that report were unsuccessful.[1]

The development of the chemistry of monocoordinate phosphorus was inhibited by the Mulliken–Pitzer hypothesis, according to which the existence of phosphorus derivatives resembling cyanides is impossible owing to the presence of vacant *d* orbitals in the phosphorus atom. Gier's study[1] disproved these views. When PH_3 was passed through a low-intensity electric arc between graphite electrodes, phosphaethyne (H−C≡P) was obtained. It is a colourless reactive gas, stable at temperatures below the triple point (−124° ± 2 °C) and at a reduced pressure (<30 mmHg).[1] The molecular weight, determined mass-spectrometrically, confirmed its composition and the addition of HCl at −110 °C with formation of dichloromethylphosphine confirmed the presence of a C≡P triple bond. The infrared spectrum of the solid specimen at −196 °C also corresponded to the H−C≡P structure.[1]

However, owing to the extreme instability of derivatives of monocoordinate phosphorus, only little attention has been devoted to their investigation during the last 15 years. Gier's data[1] have been confirmed and deuteriophosphaethyne has been obtained by an analogous procedure;[3] the microwave,[3] ultraviolet, infrared (IR), and NMR spectra[4-7] of phosphaethyne as well as its photoelectron spectrum (PES)[8] have been investigated and quantum-chemical calculations have been performed for the H−C≡P molecule.[9-11] As a result of the discovery of new methods of synthesis of phospha-alkynes, studies in this field have been developing at a higher rate only since the middle 1970's. Ten compounds of monocoordinate phosphorus and some of their deuteriated derivatives are now known; approximately 50 communications devoted to their synthesis and the study of their physicochemical properties have been published. The possibility of using phospha-alkynes in organic synthesis and in the chemistry of transition metal complexes has aroused much interest in the vigorous research into this class of OPC prosecuted at the present time.

Some information on the chemistry of phospha-alkynes is contained in reviews[12,13] devoted mainly to compounds of dicoordinate phosphorus. This review gives a systematic account and a survey of the results of studies on phospha-alkynes both in terms of the synthetic aspect and as regards their structure, physicochemical properties, and reactivity. It is noteworthy that experimental data on the synthesis and properties of phospha-alkynes have been frequently reproduced and have been confirmed by different groups of investigators. In this respect, the results of Matveev and coworkers[14-19] differ from them sharply, cannot be accepted as reliable, and are not considered in this review.

II. SYNTHESIS

Phospha-alkynes (I)–(X) (Table 1) are thermally unstable and very reactive compounds. With the exception of 3,3-dimethyl-1-phosphabutyne (VII), they are gases which are stable only at low temperatures in an inert atmosphere or at room temperature in a state of high rarefaction.

The methods of synthesis of phospha-alkynes known at present are based on the elimination of hydrogen halides, trialkylchlorosilane, or hexa-alkyldisiloxanes from substituted phosphines and compounds of dicoordinate phosphorus (phospha-alkenes). These methods can be divided into two groups: high-temperature pyrolysis and low-temperature elimination in the presence of solid alkali (Table 1). In cases where the starting compounds are di- or tri-halogenophosphines, a two-stage reaction has been proposed with formation of an intermediate phospha-alkene.

The majority of phospha-alkynes have been synthesised by high-temperature pyrolysis. Thus phosphaethyne (I) has been obtained by passing dichloromethylphosphine through a quartz tube 8 mm in diameter and 150 mm long, heated to 1000 °C, at a pressure of 2 mmHg.[20,21] 1-Phosphapropyne (II) has been synthesised analogously:[22,23]

$$MePCl_2 \xrightarrow[-HCl]{\Delta} \underset{(I)}{H-C\equiv P};$$

$$MeCH_2PCl_2 \xrightarrow[-HCl]{\Delta} [MeCH{=}PCl] \xrightarrow[-HCl]{\Delta} \underset{(II)}{Me-C\equiv P}.$$

Westwood et al.,[23] who used photoelectron spectroscopy as an

identification procedure, note that the formation of phosphapropyne (II) and HCl is not the only pathway to the decomposition of the initial dichloroethylphosphine. According to PES (the reaction products were introduced directly into the ionisation chamber of the spectrometer), the reaction mixture also contains the initial phosphine, PCl_3, C_2H_2, C_2H_4, and C_2H_6.[23] The isolation of compound (II) in a pure form therefore requires the successive employment of three low-temperature traps at −78 °C (for the separation of the initial phosphine), −126 °C (for the separation of PCl_3), and at the temperature of liquid nitrogen. When the last trap is heated, traces of C_2H_6 appear and these are followed by C_2H_4 and HCl, in order of their volatilities. Further heating yields phosphapropyne alone. Its yield is not more than 10%. As the pressure is reduced, the yield of compound (II) with respect to C_2H_4 increases. Phosphapropyne specimens can be stored without any changes at the temperature of liquid nitrogen in the course of a month.[23]

Table 1. The synthesis of phospha-alkynes (I)–(X).

Compound	Method of synthesis*	Reaction conditions		Refs.
		t, °C	p, mmHg	
HC≡P (I)	P	1000	2	[20]
DC≡P	P	1000	2	[20]
$CH_3C{\equiv}P$ (II)	P	900	0.05	[22,23]
$CD_3C{\equiv}P$	P	900	0.05	[22,23]
F—C≡P (III)	E	20	30	[32,33]
NC—C≡P (IV)	P	700	50	[20]
$CH_2{=}CH{-}C{\equiv}P$ (V)	P	1000	30—60	[24]
HC≡C–C≡P (VI)	P	1100	30—60	[25]
DC≡C–C≡P	P	1100	30—60	[25]
$Me_3C{-}C{\equiv}P$(VII)	E	20	in solution	[34]
Ph—C≡P (VIII)	P	700—800	—	[26—28]
$Me_3Si{-}C{\equiv}P$ (IX)	P	750	$2{\cdot}10^{-6}$	[29]
$CF_3C{\equiv}P$ (X)	P	—	—	[31]

*P = pyrolysis; E = elimination under the influence of alkali.

Cyanophosphaethyne (IV) has been synthesised from phosphaethyne (I).[20] The unpurified compound (I), obtained by pyrolysing dichloromethylphosphine, is passed through a trap, containing KOH pellets and cooled to −78 °C, in order to remove HCl and is then transferred together with cyanogen azide to a furnace at 700 °C and a pressure of 50 mmHg:

$$MePCl_2 \xrightarrow[-HCl]{\Delta} \underset{(I)}{HC{\equiv}P} \xrightarrow{\Delta,NCN_3} \underset{(IV)}{N{\equiv}C{-}C{\equiv}P}.$$

The authors suggest that pyrolysis of NCN_3 results in the formation of nitrile radicals which undergo a substitution reaction with phosphaethyne, giving rise to the final product (IV) in ~1% yield.[20]

Vinylphosphaethyne (V)[24] and ethynylphosphaethyne (VI)[25] have been obtained by the pyrolysis of the corresponding dichlorophosphines. In the latter case the initial phosphine is formed immediately in the reaction zone on pyrolysing a 2:1 mixture of 3-chloropropyne and phosphorus trichloride:

$$CH_2{=}CH{-}CH_2PCl_2 \xrightarrow[-HCl]{\Delta} \underset{(V)}{CH_2{=}CH{-}C{\equiv}P};$$

$$HC{\equiv}CCH_2Cl + PCl_3 \xrightarrow{\Delta} [HC{\equiv}CCH_2PCl_2] \xrightarrow{\Delta} \underset{(VI)}{HC{\equiv}C{-}C{\equiv}P}.$$

In the syntheses of phenylphosphaethyne (VIII)[26–28] and trimethylsilylphosphaethyne (IX),[29] the starting materials were compounds of dicoordinate phosphorus, both phospha-*alkynes* are formed in quantitative yields:

$$(Me)_3Si(Ph)C{=}PCl \xrightarrow[-(Me_3)SiCl]{\Delta} \underset{(VIII)}{Ph{-}C{\equiv}P};$$

$$[(Me)_3Si]_2C{=}PCl \xrightarrow[-(Me_3)SiCl]{\Delta} \underset{(IX)}{(Me)_3SiC{\equiv}P}.$$

Appel et al.[26] noted that the method of synthesis which they proposed makes it possible to isolate phenylphosphaethyne (VIII) in a pure form, which was impossible when benzyldichlorophosphine was used as the starting material owing to the large amount of impurities formed during its pyrolysis. However, even in the absence of impurities, the phospha-alkyne (VIII) is stable only at a low temperature, decomposing slowly above −50 °C (the half-life at 0 °C was 7 min).[26] The trimethylsilyl derivative (IX) is somewhat more stable and begins to decompose only at −10 °C; the half-life at room temperature is 50 min.[29] This compound can also be obtained by the pyrolysis of *P*-chlorobis(methylene)phosphorane:[30]

$$[Me_3Si]_2C{=}\overset{Cl}{\overset{|}{P}}{-}C[SiMe_3]_2 \xrightarrow{\Delta} \underset{(VIII)}{Me_3SiC{\equiv}P}.$$

The available information about the synthesis of trifluoromethylphosphaethyne (X) is extremely scanty.[31] The compound has been obtained by the pyrolysis of pentafluoroethylphosphine:

$$CF_3CF_2PH_2 \xrightarrow[-HF]{\Delta} \underset{(X)}{CF_3C{\equiv}P}.$$

The low-temperature elimination method makes it possible to synthesise phospha-alkynes which are unstable at high temperatures. Fluorophosphaethyne (III)[32,33] and 3,3-dimethyl-1-phosphabutyne (VII)[34] have been obtained in this way. Compound (III) is formed when the vapour of the initial trifluoromethylphosphine is passed through a spiral glass tube 10 mm in diameter and 400 mm long filled with solid potassium hydroxide, at room temperature and a pressure of 30 mmHg:

$$CF_3PH_2 \xrightarrow[-HF]{KOH} [CF_2{=}PH] \xrightarrow[-HF]{KOH} \underset{(III)}{FC{\equiv}P}.$$

An increase of the contact time between the initial phosphine and the alkali and a decrease of pressure lead to an increase of the content of fluorophosphaethyne (III) relative to the phospha-alkene.[32]

The initial reactant in the synthesis of the t-butyl derivative (VII) is a compound of dicoordinate phosphorus:[34]

$$\begin{matrix} Me_3SiO \\ Me_3C \end{matrix}\!\!>\!C{=}PSiMe_3 \xrightarrow[-[Me_2Si]_2O]{NaOH} \underset{(VII)}{Me_3C{-}C{\equiv}P}.$$

At room temperature solid sodium hydroxide is added slowly into a solution of the disilyl derivative in diethylene glycol dimethyl ether; the yield of compound (VII) is 76%. 3,3-Dimethyl-1-phosphabutyne (VII) is a colourless mobile liquid with a b.p. 61 °C and is the only representative of phospha-alkynes stable under normal conditions known at the present time.

The phospha-alkynes (I)–(IV), (VIII), and (IX) have been obtained by methods analogous to those described above.[35]

The high reactivity and thermal instability of phospha-alkynes precludes the synthesis of most of them by these methods in preparative amounts. Phospha-alkynes are even more unstable in the presence of the numerous impurities formed in the pyrolysis of the initial phosphines. In this sense the search for new methods of synthesis is undoubtedly an urgent problem in the chemistry of compounds of monocoordinate phosphorus.

III. STRUCTURE AND PHYSICOCHEMICAL PROPERTIES

The phospha-alkynes (I)–(X) have been investigated with the aid of various physicochemical methods: mass-spectrometry and microwave, photoelectron, IR, and NMR spectroscopy. Mass spectra have been used to identify the compounds and to determine their molecular weights. Microwave and photoelectron spectra have also been employed successfully for the same purpose. The microwave spectroscopic and PES methods, which make it possible to transfer in the course of experiments the substances from the synthetic zone directly into the spectrometer cell with rarefaction and at a low temperature, are the most convenient and in many instances the only methods available for the identification and analysis of compounds as unstable as phospha-alkynes. Because of the low stability of phospha-alkynes, IR and NMR spectroscopy are used to investigate them to a much lesser extent.

Table 2. The structural parameters of phospha-alkynes RCP.

Compound	R	$r(X^*-C_{sp})$, Å	$r(C\equiv P)$, Å	Refs.
(I)	H	1.0667	1.5421	[3, 36]
(II)	Me	1.465	1.544	[37]
(III)	F	1.285; 1.270	1.541; 1.547	[38], [32]
(IV)	NC	1.382	1.544**	[20]
(V)	CH_2=CH	1.432	1.544**	[24]
(VI)	CH≡C	1.382	1.544**	[25]
(VII)	Me_3C	1.473	1.536	[39]
(VIII)	Ph	1.467	1.544**	[28]
(X)	CF_3	1.460	1.542	[31]

*X = atom of group R linked to the C_{sp} carbon atom.
**The parameter was taken from data for compound (II).[37]

The steric structure of phospha-alkynes has been established by a microwave spectroscopy (Table 2); they are structural analogues of the corresponding nitriles. Thus, like hydrogen cyanide, phosphaethyne has a linear structure and in both molecules the shortening of the C≡P and C≡N bonds[40] relative to single C–P and C–N bonds is almost the same (0.31 and 0.32 Å). The C–N [and C–P?] bond lengths in these compounds also differ little (1.0632 Å in HCN). A similar situation has been noted also[28,37,39] for alkyl and phenyl derivatives of phosphaethyne [compounds (II), (VII), and (VIII)] and the corresponding nitriles: the values of $r(C-C_{sp})$, namely 1.458 Å in MeCN and 1.451 Å in PhCN, differ little from those for the phospha-alkynes (II) and (VIII) (Table 2). On the other hand, the F–C bond in the F–C≡P molecule is much longer than in F–C≡N (1.262 Å) and is close to the value 1.279 Å observed in the F–C≡CH molecule.[38] A characteristic feature of phospha-alkynes which distinguishes them from nitriles is a weak sensitivity of the C≡P bond length to the substituent at the carbon atom (Table 2) – some shortening of the bond is observed only for the t-butyl derivative (VII). It has been noted[39] that, although the opposite tendency is observed in the series of a corresponding nitriles [$r(C\equiv N)$, Å: 1.156 in HCN, 1.157 in MeCN, and 1.159 in Me_3CCN], it is difficult to draw definite conclusions on this basis because of the assumptions made for phospha-alkynes (see the footnote to Table 2) and the possible experimental errors. However, the main tasks in the analysis of microwave spectra, namely the identification of representatives of the new class of OPC and an unambiguous demonstration of the structure with a C≡P triple bond, have been carried out.

Six phospha-alkynes have been investigated by PES (Table 3). In all the compounds, the first ionisation potential (IP) corresponds to the removal of an electron from a bonding π orbital localised predominantly at the C≡P group and the second ionisation potential corresponds to the removal of a non-bonding *n* electron localised at the phosphorus atom. The results of a comparative analysis of the PES of phospha-alkynes and the corresponding nitriles indicate the similarity of the electronic structures of the RC≡P and RC≡N molecules.[41] This is shown, for example, by the influence of substituents on the orbital characteristics, which are virtually identical in the series of phospha-alkynes and nitrides (Fig.1). Thus the stabilisation of the bonding π orbital is observed in both series and the observed order in the variation of the π(C≡)IP, namely H > F > Me > Me_3C, is due to the mesomeric (+*M*) effect of the substituents.[41] In both phospha-alkynes and nitriles, the IP of the *n* orbital decreases consistently in the sequence R = F, H, Me, Me_3C, in conformity with the increase of the +*I* effect of the substituent R.[41] On the other hand, in all the phospha-alkynes there is a greater shift towards lower ionisation potentials compared with nitriles than might have been supposed to result from substitution of the nitrogen atom by the less electronegative phosphorus atom.[41] Evidently the most important feature of phospha-alkynes is the increase in the latter of the $\pi - n$ separation compared with nitriles, which is a quantitative indication of the decrease of the $2p\pi-3p\pi$ overlap in these compounds compared with the $2p\pi-2p\pi$ overlap in the RC≡N molecules.[41] These data are clearly illustrated by the correlation orbital diagram (Fig.1).[41] The difference in the separation of the π and *n* levels between phospha-alkynes and nitriles noted above is manifested also in their chemical properties (Section IV).

Table 3. PES data for phospha-alkynes RCP.

Compound	R	IP[π(C≡P)], eV	IP[*n*(P)], eV	Refs.	Compound	R	IP[π(C≡P)], eV	IP[*n*(P)], eV	Refs.
(I)	H	10.79	12.86	[8]	(VII)	Me_3C	9.61	11.44	[41]
(II)	Me	9.89	12.19	[23]	(VIII)	Ph	8.68	11.76	[41]
(III)	F	10.57	13.55	[32]	(IX)	Me_3Si	9.9	10.9	[42]

There is very little information about the IR spectra of phospha-alkynes, probably because of experimental difficulties. The ν(C≡P) stretching vibration frequency varies within fairly broad limits: 1265 cm^{-1} for HC≡P,[1] 1660 cm^{-1} [33] or 1670.8 cm^{-1} [43] for FC≡P, and 1533 cm^{-1} for $Me_3C-C\equiv P$.[34] There are contradictions in the literature data for ν(C≡P) in the infrared spectrum of phosphaethyne. Johns et al.[4] altogether failed to observe the band at 1265 cm^{-1} and concluded that its assignment to ν(C≡P) was erroneous. A similar doubt was expressed also by Becker et al.[34] in connection with a comparison of the IR spectra of HC≡P[1] and $Me_3CC\equiv P$. In the light of the available limited data, the ν(C≡P) band in the IR spectra of phospha-alkynes appears to be non-characteristic.

Studies of the phospha-alkynes (I), (III), and (VII)–(IX) by ^{31}P and ^{13}C NMR have shown (Table 4) that, whereas the range of variation of the chemical shift of the signal due to the phosphorus nucleus in these compounds is about 300

p.p.m., the $\delta^{13}C$ chemical shift for the *sp*-hybridised carbon atom is more characteristic ($\Delta\delta \cong 50$ p.p.m.). It has been noted[7] that the spin–spin coupling constant $^1J(CH) = 211$ Hz in the ^{13}C NMR spectrum of phosphaethyne is directly related to the nature of the C≡P triple bond and shows that the hybridisation of the carbon atom in the HC≡P molecule is close to *sp* (calculation yields 43% of *s* character).

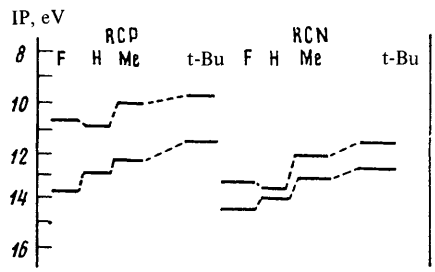


Figure 1. Orbital correlation diagram for the first two ionisation potentials of RCP and RCN.[41]

Table 4. NMR data for phospha-alkynes RCP.

Compound	R	$\delta^{31}P$, p.p.m.*	$\delta^{13}C_{sp}$, p.p.m.**	$^1J(P\text{-}C_{sp})$, Hz	Refs.
(I)	H	−32	154	54	[7]
(III)	F	−206.4	—	—	[33]
(VII)	Me_3C	−69.2	184.8	38.5	[34]
VIII	Ph	−32	164.9	48.3	[26]
(IX)	Me_3Si	96	201.4	13.9	[29]

*Relative to 85% H_3PO_4.
**Relative to Me_4Si.

Important information about the polarity of phospha-alkynes has been obtained in their investigation by microwave spectroscopy. The experimental dipole moments of the compounds (μ_{exp}, D) are 0.39 for HCP,[3] 1.499 for MeCP,[37] 0.279 for FCP,[38] 3.44 for NCCP,[20] 1.183 for CH_2 = CHCP,[24] and 0.745 for HC≡CCP.[25] The significant difference between the dipole moments of HCP and HCN (μ_{exp} = 3 D) has been explained[3] by the lower electronegativity of the phosphorus atom compared with the nitrogen atom (2.1 and 3.0 respectively) and by the diffuseness of the unshared (lone) electron pair (LEP) of the phosphorus atom. Analysis of the dipole moments of the phospha-alkynes (I)–(VI) in terms of the vector-additive scheme made it possible to determine the polarity of the C≡P triple bond.[44] It has been noted[44] that the data for the polarity of the phospha-alkynes fit satisfactorily within the framework of the additive computational scheme after the correct selection of the corresponding models despite the view[20] that there are no signs of additivity. The polarity of the C≡P bond is almost independent of the substituent at the *sp* hybridised carbon atom and is characterised by a dipole moment of 0.7 ± 0.1 D in the direction from phosphorus to carbon. The opposite polarity of the C≡P bond in phospha-alkynes compared with the C≡N bond in nitriles is also indicated by the results of a quantum-chemical calculation for the HCP molecule,[10] according to which the carbon atom constitutes the negative end of the C≡P bond dipole: the charges on the H, C, and P atoms are respectively +0.226 e, −0.307 e, and +0.081 e.

IV. CHEMICAL PROPERTIES

The chemical properties of phospha-alkynes have been little investigated. It is known that these compounds rapidly polymerise on raising the temperature, forming solid resins.[1] At temperatures somewhat above those corresponding to their stability, phospha-alkynes interact with hydrogen halides to form halogenophosphines and phospha-alkenes:[1,26]

$$\underset{(I)}{H{-}C{\equiv}P} + HCl \xrightarrow{-110^\circ} MePCl_2;$$

$$\underset{(VIII)}{Ph{-}C{\equiv}P} + HCl \rightarrow PhCH{=}PCl.$$

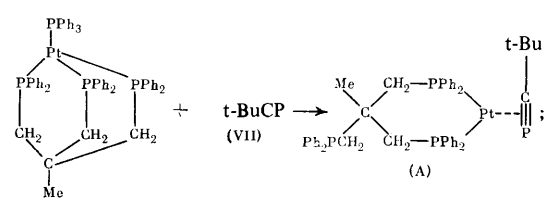
These reactions have been used to demonstrate the structure of the phospha-alkynes (I)[1] and (VIII)[26] obtained. In many of the studies quoted above the possibility of using phospha-alkynes in synthetic chemistry and in the transition metal complex chemistry is discussed. For example, it has been suggested that, owing to the large positive charge on the phosphorus atom (+0.48 e on P, −0.09 e on C, and −0.39 e on F), fluorophosphaethyne can function as an electron density acceptor in chemical reactions.[32] However, the low thermal stability of phospha-alkynes and the impossibility of synthesising them in preparative amounts preclude their wide-scale employment in practical chemistry. Only a series of transition metal complexes of the only phospha-alkyne stable under normal conditions, namely the t-butyl derivative of compound (VII),[45–49] and the cycloaddition reaction involving PhC≡P[27] have so far been investigated.

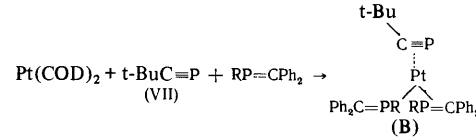
3,3-Dimethyl-1-phosphabutyne taken in excess forms cream-coloured semitransparent crystals of a 1:1 complex with zerovalent platinum at room temperature in benzene in a quantitative yield:[45]

$$Pt(C_2H_4)(PPh_3)_2 + t\text{-}BuC{\equiv}P \rightarrow Pt(PPh_3)_2(t\text{-}BuC{\equiv}P).$$

X-Ray diffraction analysis of the complex showed that the phospha-alkyne (VII) is coordinated "sideways" to the platinum atom, so that the LPE of the phosphorus atom hardly interacts with the metal (Fig. 2).[45] It was of interest that the C–P bond (1.672 Å) in the coordinated t-BuCP is appreciably longer than that in the free molecule of compound (VII) (1.544 Å). Elemental analysis of the ^{31}P NMR spectra of the complex are consistent with the structure presented.[45]

The synthesis of two new complexes of t-BuCP with zerovalent platinum, in which the phospha-alkyne is also coordinated "sideways" to the platinum atom, has been recently reported:[46,47]





Here COD = cyclo-octa-1,5-diene and R = mesityl. Structure (B) is the first example of a complex containing only

phospha-alkyne and phospha-alkene molecules as ligands, both molecules of the latter compound being coordinated to the platinum atom via the LEP of the phosphorus atom, in contrast to t-BuC≡P. A characteristic feature of the NMR spectra of all three complexes of compound (VII) with zerovalent platinum is the very low spin–spin coupling constant ^1J(Pt, P), which is 62 Hz for $Pt(PPh_3)_2$(t-BuCP),[45] 144 Hz for structure (A), and 115 Hz for structure (B),[46] which indicates a greater amount of *s* character of the LEP of the phosphorus atom in the coordinated phospha-alkyne (VII).[46]

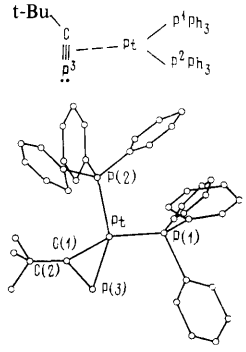
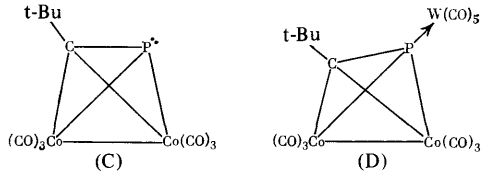


Figure 2. The structure of the complex of t-BuCP with zerovalent platinum.[45]

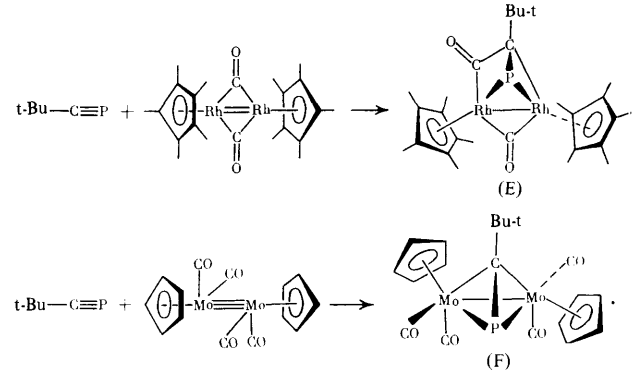
Equimolar amounts of t-BuCP and $Co_2(CO)_8$ react in tetrahydrofuran at room temperature with formation of the complex $Co_2(CO)_6$(t-BuCP) (C); it is a blood-red oil, which readily decomposes in air and in the light.[46] When the reaction is carried out in toluene with subsequent addition of tungsten pentacarbonyl, the crystalline complex $Co_2(CO)_6$(t-BuCP). .$W(CO)_6$ (D), which is stable in air and has m.p. 109–110 °C, is formed:[48]



Its structure, in which t-BuCP is a donor of six electrons, has been established by X-ray diffraction:[48] the bridging phospha-alkyne fragment and the two $Co(CO)_3$ groups form a tetrahedron, the phosphorus atom being coordinated to $W(CO)_5$. The C–P bond in the coordinated phospha-alkyne (VII) (1.695 Å) is much longer, as in the platinum complex, than in the free ligand. The shorter W–P bond in this complex compared with that in the familiar complex cis-$W(CO)_4$. .$(PMe_3)_2$ (2.502 Å) reflects, according to the authors,[48] an unusual hybridisation of the phosphorus atom in complex (D).

At −60 °C t-BuCP adds quantitatively to the metal–metal Rh=Rh and Mo≡Mo multiple bonds with formation of complexes (E) and (F), which are resistant to oxygen and atmospheric moisture:[49]

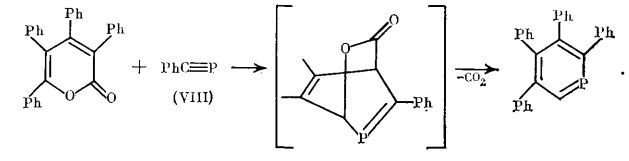
Scheme



The addition takes place in both cases at right angles to the metal–metal bond. X-Ray diffraction analysis of complex (F) showed[49] that its molecule contains the Mo_2PC tetrahedron; the length of the P–C bond increases to 1.713 Å, which is characteristic of a double bond.

The chemistry of the complexes of phospha-alkynes with transition metals constitutes a clear manifestation of an important feature of their electronic structure, noted in the analysis of the PES:[41] the much more significant separation of the π and *n* levels in phospha-alkynes than in nitriles. It is known for the majority of nitriles that they are coordinated to transition metals via the LEP of the nitrogen atom and that only some of them, having a powerful electron-accepting group at the carbon atom (for example, $CF_3C{\equiv}N$) add "sideways".[41] On the other hand, the coordination of the metal to the C≡P triple bond is characteristic of phospha-alkynes. The unshared electron pair of the phosphorus atom is involved only in complex (D) on formation of a bond with a tungsten atom, because the possibilities for coordination with participation of the π electrons of the C≡P bond have already been exhausted.[48]

An example of the involvement of a phospha-alkyne as a dienophile in the diene synthesis is provided by the [4 + 2]-cycloaddition of phenylphosphaethyne to α-pyrone and cyclopentadienone.[27] In both cases PhCP reacts at the instant of its evolution on thermolysis of the phospha-alkene $Ph(Me_3Si)C$ = PCl with the corresponding diene to form λ^3-phosphorines after the elimination of CO_2 or CO,[27] for example:



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The data presented illustrate the first advances achieved in the chemistry of derivatives of monocoordinate phosphorus. The search for new methods of synthesis of stable phospha-alkynes and the improvement of the physicochemical experimental techniques will undoubtedly promote further successful development of research into this new and interesting field of the chemistry of OPC.

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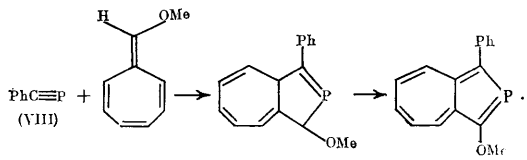
During the preparation of the manuscript for the press, several new publications appeared on the subject of this review.[50–52] A study of the PES of phosphaethyne and fluorophosphaethyne by the method of Green functions

showed that the ionisation of the 1π and 3σ MO in HCP and also of the 2π, 4σ, and 1π MO in FCP can be described within the framework of a one-particle ionisation pattern.[50] The vibrational-rotational spectrum of fluorophosphaethyne has been investigated.[51] The observed frequency $\nu(C\equiv P) = 1670.842\ cm^{-1}$ agrees with $\nu(C\equiv P) = 1670.8\ cm^{-1}$ determined previously.[43]

The reaction involving the [8 + 2]-cycloaddition of phenylphosphaethyne to 8-methoxyheptafulvene leads to the formation of the previously unknown 2-phospha-azulene:[52]



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Substituted Ureas. Methods of Synthesis and Applications

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Systematic data on the method of synthesis of ureas by the interaction of compounds containing the amino-group with organic isocyanates, of amines and alkyl halides with alkali metal cyanates, and of primary and secondary amines with phosgene, carbon dioxide, urea, or nitrourea and by the carbonylation of amines are presented. The reactions involving the alkylation of urea and its interaction with various compounds containing functional groups are considered. The advantages and disadvantages of various methods are noted. The principal and practical applications of substituted ureas, including their applications as additives to organic materials, are discussed.
The bibliography includes 314 references.

CONTENTS

I. Introduction 249
II. Methods of synthesis of substituted ureas 249
III. Applications of substituted ureas 254

I. INTRODUCTION

Substituted ureas have attracted attention because of the wide variety of their applications in industry, engineering, agriculture, and medicine;[1] they are widely used as pesticides and plant growth regulators, are effective additives, for different purposes, to hydrocarbon fuels and oils and polymeric materials, and they have found applications as medicinal preparations and dyes.

An enormous amount of factual data has now been accumulated on the methods of synthesis, properties, and applications of substituted ureas. However, hitherto there have been no review articles in the literature devoted to these compounds.

Kutepov's review[2] covers the literature up to 1961 and deals with the synthesis and reactions of only one group of compounds of this type—diarylureas. A review[3] dealing with the methods of synthesis, structure, and properties of a specific class of ureas, namely carbohydrate derivatives with carbamide fragments, was published in 1982. For this reason, carbohydrates containing derivatives of urea are not dealt with in this review.

The present communication is the first attempt at a survey and systematic account of the available literature data and the methods of synthesis and practical applications of substituted ureas.

II. METHODS OF SYNTHESIS OF SUBSTITUTED UREAS

The methods for the preparation of substituted ureas developed at the present time can be divided into eight principal groups.

1. The Interaction of Amino-compounds with Organic Isocyanates

In 1848 Würtz obtained symmetrical dimethylurea for the first time by treating methyl isocyanate with water.[4,5] Subsequently these results were confirmed: the corresponding symmetrical dialkylureas were obtained by decomposing methyl, ethyl, butyl, and isobutyl isocyanates with water.[6] The corresponding amines are formed as intermediates in these processes, reacting further with another isocyanate molecule:

$$RNCO \xrightarrow{H_2O} RNHCOOH \xrightarrow[-CO_2]{} RNH_2 \xrightarrow{RNCO} RNHCONHR .$$

The method has been used to synthesise substituted di(isocyanatophenyl)ureas by the reaction of 1-R-substituted 2,4-phenylene di-isocyanates with water in molar proportions of 2 : 1 and using ether as the solvent.[7]

The interaction of organic isocyanate with amines, for example, of phenyl isocyanate with methylaniline, ethylaniline, or diphenylaniline, leads to substituted ureas:[8]

$$C_6H_5NHR + C_6H_5NCO \rightarrow C_6H_5N(R)CONHC_6H_5 ;$$
$$R = CH_3,\ C_2H_5,\ C_6H_5 .$$

Table 1. The isocyanate method of synthesis of substituted ureas.

Initial compound	References
Amino-compounds	
Ammonia	[29—31]
Primary amines:	
saturated aliphatic	[12,15,32,33]
unsaturated aliphatic	[34]
aromatic	[8,23—25,32,35—39]
heterocyclic	[24,26,28,40—42]
Secondary amines:	
unsaturated aliphatic	[20]
saturated aliphatic	[12,14,15,18,20,43—53]
aromatic	[8]
heterocyclic	[28,54]
Alkoxyamines	[17—20]
Hydroxylamines	[9—16]
Aminophenols	[35,55—57]
Aminoalcohols	[57]
Diamines	[41,58,59]
Aminoethylbenzoxazole	[26]
Acid amides	[22,37]
Thiadazole	[27]
Organic isocyanates	
Saturated aliphatic	[4—6,10,26,27,29,31,32,35,40, 47—52,54,57]
Aromatic	[8,9,11,12,14—22,24,26,28,32,36—38, 41,43—45,53,55,56,58—60]
Saturated carbocyclic	[61]
Benzoyl isocyanate	[23,37,39]
Alkylphenylene isocyanates	[7]
Heterocyclic	[24]

The interaction of organic isocyanates with amines is nowadays the most widely used method of synthesis of asymmetric ureas. Various compounds containing the amino-group can enter into this reaction (Table 1). The reaction of alkyl isocyanates with hydroxylamines is widely used to obtain urea derivatives containing the hydroxy- or methoxy-group at one of the nitrogen atoms.[9-16]

The range of organic isocyanates used in this method is also extremely varied (Table 1).

The interaction of isocyanates with compounds containing the amino-group is as a rule carried out at room temperature or with cooling, sometimes with heating.[18,21-28] Equimolar amounts of the reactants or a slight excess of the organic isocyanates, more rarely an excess of the compounds containing the amino-group, are usually employed.

The process is normally performed in an organic solvent—benzene,[12,17-19,38] toluene,[14,25,39] xylene,[25] cresol,[23,24,53] chlorobenzene and dichlorobenzene,[12,25,52] methyl or ethyl alcohol,[54] dioxan,[23,52] tetrahydrofuran,[30,37,52,54,58] dimethylformamide (DMF),[19,22] ethanolamine,[27] acetonitrile,[13,30] and methylene chloride.[59,60] Water is sometimes used as the solvent because isocyanates react with water much more slowly than with amines.

The reaction of organic isocyanates with substituted amines proceed as a rule with high yields of substituted ureas, which are frequently nearly quantitative. However, it has been noted that secondary aliphatic-aromatic amines react with isocyanates to form unstable products, which decompose on heating. Diphenylamine does not react with isocyanates.[8]

It has been established that the molecular weight of the initial amine is only slightly reflected in the rate of its reaction with isocyanates. Aliphatic amines react much faster than aromatic amines. The reactivity of the isocyanate increases with increase of the electrophilicity of the substituent in its molecule.[44]

In order to improve the mass exchange between the individual components of the reaction mixture, *N*-aryl-*N'N'*-dimethylureas, where aryl = phenyl or *p*-chlorophenyl, have been synthesised in the presence of surfactants.[43] The yield of, for example, *N*-phenyl-*N'N'*-dimethylurea then amounted to 97.5%.[44]

Kinetic studies of the reactions of isocyanates with amines have been carried out.[62-67] The influence of substituents in the molecules of the isocyanate and the amine on the rate of reaction has been described and the reaction kinetics have been determined. However, hitherto there is no unanimous view concerning the reaction mechanism. It is believed[68] that the reaction proceeds in two stages. The first stage involves the formation of an activated complex, which is subsequently converted into the substituted urea by reacting with the amine. By analogy with the scheme proposed by Zahradnik,[69] the rearrangement of the intermediate complex into urea may be regarded as possible in principle:

$$RNCO + R'NH_2 \rightleftarrows \left[RN{=}C^{+}{-}O^{-} \cdots H_2NR' \right] \rightleftarrows \left[RN{=}C\begin{matrix} O^{-} \\ \diagdown \\ NH_2^{+} \cdots R' \end{matrix} \right] \rightarrow RNHC\begin{matrix} O \\ \diagdown \\ NHR' \end{matrix}$$

The thermodynamic data presented by Vorob'ev et al.[70] allow the possibility of the formation of a four-centre activated intermediate complex:

$$\begin{matrix} RN{=}C{=}O \\ H{-}NH{-}R' \end{matrix} \rightarrow \left[\begin{matrix} R{-}N{-}C{=}O \\ \vdots \quad | \\ H \cdots NHR' \end{matrix} \right] \rightarrow \begin{matrix} RN{-}C{=}O \\ | \quad | \\ H \quad NHR' \end{matrix}$$

2. The Interaction of Amines and Alkyl Halides with Alkali Metal Cyanates

Cyanic acid and alkali metal cyanates are fairly frequently used to obtain substituted ureas.[71-75] Würtz proposed for the first time in 1851 the alkylureas be obtained by evaporating to dryness a solution of the sulphuric acid salt of the corresponding amine and potassium cyanate.[71]

Subsequently the cyanate method of synthesis of substituted ureas was used in a number of investigations.[72-75] In particular, a large number of arylureas were obtained[72,73] by the reaction of the arylamine hydrochloride with sodium cyanate at 30 °C in glacial acetic acid with their subsequent separation in the form of a water-insoluble precipitate.

The reaction of alkyl halides with cyanate in aqueous DMF, described for the first time by Fukui et al.,[76] is a variety of the cyanate method of synthesis. The authors established that the composition of the reaction product is determined mainly by the presence of water in the reaction mixture. Thus, when dried reagents are used, only tributyl isocyanurate was obtained from butyl bromide in 84% yield, while in the presence of added water (0.56 of a mole per mole of butyl bromide) the yield of tributyl isocyanurate was 7% and that of symmetrical dibutylurea was 75%.[76]

The influence of the structure of the initial alkyl halide on the yield of substituted ureas has been investigated[77] and it has been established that the best yields of the required products are achieved when primary alkyl halides with a straight chain are employed; tertiary alkyl halides do not react. For example, unbranched alkyl bromides and alkyl chlorides react with potassium cyanate at 100–130 °C in DMF in the presence of an equimolar amount of water to form *NN*-dialkylureas in 90–96% yield.

By treating an alkyl chloride with potassium cyanate in DMF containing 5% of water at 100 °C, Argabright et al.[78] obtained monosubstituted ureas as well as the *NN*-disubstituted derivatives. The 1,5-disubstituted biuret is then formed as a side product and the formation of the 1,3,5-trisubstituted isocyanurate is not observed.

3. The Interaction of Primary and Secondary Amines with Phosgene

Symmetrical dialkyl-, diaryl-, and alkylaryl-ureas are obtained by treating the corresponding amines with phosgene. Several reviews devoted to the chemistry of phosgene, in particular its interaction with amines, are available.[44,67,79-84]

By passing phosgene through a saturated aqueous solution of aniline, Hoffman obtained for the first time diphenylurea:[85]

$$C_6H_5NH_2 + COCl_2 \rightarrow C_6H_5NHCONHC_6H_5 + HCl\ .$$

The reaction of phosgene with aniline was investigated by Japanese workers,[86] who established that aniline hydrochloride and the chloride of phenylcarbamic acid are formed together with diphenylurea.

Starting in 1875, Michler[87-92] began publishing communications on the treatment of primary and secondary amines with phosgene. Thus, by treating diphenylamine with phosgene in ligroin, he obtained diphenylcarbamoyl chloride $(C_6H_5)_2N{-}C\begin{matrix} O \\ \diagdown \\ Cl \end{matrix}$, which readily reacts with the initial amine to form a substituted urea. Thus it has been established that the reaction between the amine and phosgene proceeds in two stages, the hydrogen chloride evolved being combined with the amine to form the amine hydrochloride:

$$RR'NH + COCl_2 \rightarrow RR'NCOCl + RR'NH \cdot HCl\ ;$$
$$RR'NCOCl + RR'NH \rightarrow RR'N{-}CO{-}NRR' + RR'NH{\cdot}HCl\ .$$

Treatment of aqueous solutions of amines with a benzene solution of phosgene in the presence of alkali led to dimethyl-, diethyl-, and difurfuryl-ureas in quantitative yields.[93] In subsequent studies it was shown[94,95] that the reaction takes place successfully not only in aqueous solution but also in organic solvents.

In many instances it has been suggested that, in order to increase the yield of a substituted urea, the hydrogen chloride evolved during its synthesis be absorbed with the aid of special acceptor additives.[93,96-101] Alkalis, sodium and calcium carbonates, sodium acetate, and zinc and magnesium oxides[94,96-98] are used as hydrogen chloride acceptors in an aqueous medium, while in organic solvents the acceptors are triethylamine, dimethylaniline,[99-101] and other tertiary amines.

The literature data[84,102-107] show that the rate of reaction of amines with phosgene is extremely high and increases with increasing basicity of the initial amine. Kutepov and Rozanova were the first to investigate the mechanism of the reaction between phosgene and amines.[108,109] They believe that in the first stage of the reaction the nucleophile (the amine) adds to the powerful electrophile (phosgene) to form a 1:1 or 2:1 complex depending on the reactant ratio. The complex, being unstable, decomposes to form an *N*-substituted carbamoyl chloride or a di-*N*-substituted symmetrical urea. The carbamoyl chloride formed from the 1:1 adduct can split off hydrogen chloride to form the isocyanate. At the same time the carbamoyl chloride and the isocyanate formed from it interact with the amine to form a di-*N*-substituted symmetrical urea.

Japanese investigators[110] showed that the interaction of phosgene (in 10% excess) with aromatic amines (aniline, *p*-toluidine, and *p*-nitroaniline) and their hydrochlorides results in the rapid formation of the *N*-arylcarbamoyl chloride and the amine hydrochloride even at −15 °C. Only at temperatures above 0 °C do appreciable amounts of the diarylurea appear.

Other communications have also been devoted to the treatment of amines and their hydrochlorides with phosgene.[111-115] The most thorough studies on the treatment of primary, secondary, and tertiary amines with phosgene have been carried out by Strepikheev and co-workers,[67,116] who investigated the kinetics of the interaction of amines with phosgene and established that it is a complex chemical process consisting of several parallel-consecutive reactions.

In contrast to Kutepov and Rozanova, the authors believe that amines are not acylated directly on treatment with carbamoyl chlorides, but convert the latter into isocyanates:

$$RNHCOCl + RNH_2 \rightarrow RNH_3Cl + RNCO .$$

The free isocyanate then reacts with the excess amine to form a disubstituted urea.

The formation of ureas on treatment of amines with phosgene proceeds in accordance with the following scheme:

$$RNH_2 + COCl_2 \rightarrow RNHCOCl + HCl ; \quad (1)$$

$$RNH_2 + HCl \rightarrow RNH_3Cl ; \quad (2)$$

$$RNH_2 + RNHCOCl \rightarrow RNH_3Cl + RNCO ; \quad (3)$$

$$RNHCOCl \rightleftarrows RNCO + HCl ; \quad (4)$$

$$RNHCOCl + RNH_2 \rightarrow [RNCO] \rightarrow (RNH)_2CO ; \quad (5)$$

$$RNH_2 + RNCO \rightarrow (RNH)_2CO . \quad (6)$$

The amine hydrochlorides and disubstituted symmetrical ureas also react with phosgene to form the corresponding carbamoyl chlorides:

$$RNH_3Cl + COCl_2 \rightarrow RNHCOCl + HCl ; \quad (7)$$

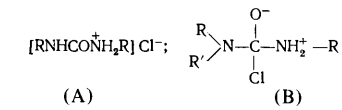
$$(RNH)_2CO + COCl_2 \rightarrow RNHCOCl . \quad (8)$$

In addition the isocyanates can polymerise [reaction (9)] and in certain cases the NCO group can be replaced by chlorine:

$$n\,RNCO \rightarrow (RNCO)_n . \quad (9)$$

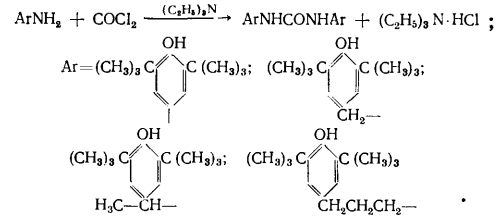
In the presence of an excess of phosgene substituted ureas are absent from the reaction mixture, which indicates a relatively low rate of reactions (5) and (6) compared with reactions (1) and (2). Consequently, in order to increase the yield of substituted ureas, it is necessary to use an excess of the amine and, in order to increase the rate of reaction, a hydrogen chloride acceptor must be employed.

Thus substituted ureas are obtained on treatment with phosgene as a result of the interaction of amines with intermediates—isocyanates and carbamoyl chlorides. Reviews concerning the mechanism of the last reaction are contradictory. The ammonide salts (A)[109] or the dipolar ions (B)[117,118] have been proposed as intermediates:



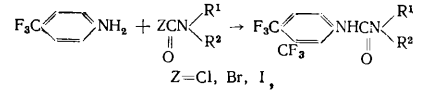
(A) (B)

Symmetrically disubstituted ureas can be obtained by treating sterically hindered aminophenols with phosgene in solution in benzene in the presence of triethylamine as the hydrogen chloride acceptor:[56]



The yield of substituted ureas decreases from 85 to 66% on passing from 4-aminophenol to 4-hydroxyphenylpropylamine. Together with substituted ureas, carbamoyl chlorides ArNHCOCl were isolated; the reaction proceeds via the intermediate formation of these compounds.

Some workers have suggested that substituted ureas be obtained by the reaction of amines with carbamoyl chlorides.[45,87,92,119] Thus *N'*-alkyl-*NN*-diphenylureas have been obtained in 90–98% yields from diphenylcarbamoyl chloride in an aqueous solution of C_2–C_4 alkylamines in acetone or toluene using hydrogen chloride acceptors—a tertiary amine or inorganic bases.[119] The corresponding ureas have been synthesised by the reaction of 3,4-bis(trifluoromethyl)aniline with dialkylcarbamoyl halides:[45]



where R^1 = H, a lower alkyl, alkenyl, or alkoxy-group and R^2 = a lower alkyl or alkenyl.

Substituted ureas containing a hydroxy-group at one of the nitrogen atoms have been obtained in satisfactory yields by the reaction of arylhydroxylamines with dialkylcarbamoyl chlorides.[9]

4. The Interaction of Amines with Urea and Nitrourea

Substituted ureas have been obtained in 50–80% yields by fusing urea together with amine hydrochlorides at ~180 °C or by refluxing in aqueous solution.[120-123] It has been

established that urea dissociates into ammonia and isocyanic acid, which reacts with the primary amine to give a monosubstituted urea; the latter splits off ammonia and is converted into the isocyanate, which again reacts with the amine to form a disubstituted urea:

$$H_2NCONH_2 \xrightarrow[-NH_3]{} HNCO \xrightarrow{RNH_2} RNHCONH_2 \xrightarrow[-NH_3]{} RNCO \xrightarrow{RNH_2} RNHCONHR .$$

It has been noted[124] that, by varying the amine : urea ratio, it is possible to obtain predominantly monosubstituted ureas.

Diphenylureas have been obtained by heating one part of urea with three parts of aniline at 150–170 °C.[125]

The study of various methods of synthesis of *NN'*-dimethylurea showed that the highest yield of the latter (80–90%) is obtained when methylamine reacts with urea.[126]

The method developed by Davis and co-workers[120–122] was subsequently widely used to synthesise *N*-alkyl(aryl)- and *NN'*-dialkyl(diaryl)ureas.[127–130] In order to increase the yield of substituted ureas, some workers recommend that the reaction be carried out between urea and amines in high-boiling solvents (cyclohexanol, phenol, or decalin[131–133]) or that the initial urea be made to interact with aqueous solutions of amine hydrosulphates or hydrophosphates.[134] Sometimes,[135] in order to obtain *NN*-dialkylureas of high purity, the reaction between urea and dimethyl- or diethyl-amine is carried out in an aqueous medium at 120–140 °C under pressure.

Asymmetric ureas are synthesised by transamination, for example, by the reaction of diarylurea with dimethylamine.[136]

A convenient method of synthesis of substituted ureas involves the reaction of amines with nitrourea.[137–140] Like urea, nitrourea is cleaved on heating with formation of isocyanic acid and nitramide:[137]

$$NH_2CONHNO_2 \rightarrow HNCO + H_2NNO_2 .$$

Since the nitro-group is an electron acceptor, nitrourea decomposes faster than urea. The corresponding substituted ureas have been obtained in 80–90% yields by the reaction of primary and secondary amines with nitrourea,[137] the yields being 10–30% higher than in the case of urea. It is noteworthy that nitramide, which decomposes into water and nitrous oxide under the conditions of the synthesis, promotes the shift of the equilibrium towards the formation of isocyanic acid and ultimately the formation of substituted ureas. Various substituted ureas have been obtained in 75–95% yields by the interaction of equimolar amounts of nitrourea with monoalkyl-, dialkyl-, and alkyl-aryl-amines in water.[138]

If the reaction between amines and nitrourea is carried out in 95% ethanol instead of water, then the yields of substituted ureas increase by 20–40%. The method is particularly effective when the solubilities of the initial amines in water are limited.[139]

N-Substituted ureas having the general formula $C_6H_5ZCH_2NHCONH_2$ (Z = cyclopropylene, cycolhexylene, or cyclopentylene) have been obtained by the method of Davis and Blanchard[137] in 30–50% yields.[140] A large number of substituted ureas have been synthesised by the reaction of sterically hindered aminophenols with nitrourea.[141]

Nitrosomethylurea also reacts with amines analogously to urea and nitrourea.[142] A series of *N*-alkylureas have been obtained in 70–90% yields with its aid:[142]

$$CH_3N(NO)CONH_2 \rightarrow CH_3NHNO + HNCO ;$$
$$CH_3NHNO \rightarrow N_2O + CH_3OH ;$$
$$HNCO + RNH_2 \rightarrow RNHCONH_2 .$$

5. The Interaction of Urea with Various Compounds

The methods of synthesis of *N*-alkyl and *NN*-dialkyl-ureas by the reaction of aldehydes and ketones with urea under oxygen pressure in the presence of nickel and cobalt catalysts are of interest.[143–145] The reaction is carried out at 60–150 °C, *N*-alkylurea and *NN*-dialkylurea being formed preferentially at 60–100° and 100–150 °C respectively. Thus 4-octadecylurea has been obtained in 75% yield from stearaldehyde[143] and s-butylurea has been obtained from ethyl methyl ketone in 77% yield.[145]

Mono- and di-alkylureas with an alkyl substituent having the iso-structure can by synthesised by the direct alkylation of urea with alcohols or olefins.[146–151] Thus a patent[146] suggests that urea be alkylated by tertiary alcohols using urea : alcohol : sulphuric acid (concentration 94% and above) molar ratios of 1 : 2 : 2. According to another patent,[147] the initial urea is to be alkylated by olefins containing a double bond at a tertiary carbon atom at 0 °C and using olefin : urea : sulphuric acid (90–100%) molar ratios of 1 : 4–5 : 2–2.5.

Different t-alkylureas have been obtained by the direct alkylation of urea with olefins in the presence of concentrated sulphuric acid as the catalyst,[148,149,152] The study of the reaction conditions showed that the best yield of alkylation products is achieved at temperatures between 0° and −5 °C, a sulphuric acid concentration of 96%, for molar ratios of urea, sulphuric acid, and the olefin of 1 : 2 : 4, and for a reaction time of 4–5 h.

The authors suggest that the alkylation of urea by olefins in the presence of sulphuric acid proceeds in two stages: an alkylsulphuric acid is formed in the first stage and alkylates urea further with regeneration of sulphuric acid.

In order to reduce the amount of sulphuric acid necessary for the reaction, it has been suggested[150] that some of it be replaced by $FeSO_4.7H_2O$.

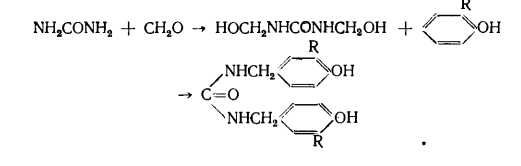
The use of a mixture of concentrated H_2SO_4 and methyl sulphate as the catalyst made it possible to obtain, by alkylating urea with isobutene, *NN'*-di(t-butyl)urea in 76.7% yield or *N*-t-butylurea in 29.6% yield relative to the initial urea.[151]

Certain symmetrical dibenzylureas are obtained by condensing phenols with urea and formaldehyde in the presence of acid catalysts.[152,155] The condensation of urea with formaldehyde to form mono(hydroxymethyl)urea in the first stage has been suggested:[155]

$$NH_2CONH_2 + CH_2O \rightarrow NH_2CONHCH_2OH .$$

The subsequent condensation with phenol in the presence of formic acid leads to *NN'*-di(4-hydroxybenzyl)urea.[155] Under these conditions, di(4-hydroxyphenyl)-methane is formed as a side product. The authors note that *N*-4-hydroxybenzylurea was not detected in any of the experiments.[155] On raising the temperature of the synthesis or on employing as the catalyst an acid stronger than formic, for example, hydrochloric, the formation of polymeric products sparingly soluble in organic solvents was observed.[155]

Alkylphenols have been condensed with urea and formaldehyde[153–155] in dearomatised petrol at 96–98 °C using 0.01% of concentrated hydrochloric acid as the catalyst. A large number of different *NN'*-dibenzylureas have been synthesised by this method in high yields:



An analogous reaction has been carried out with 2,6-di(t-butyl)phenol (DTBP).[56] In this process di[3,5-di(t-butyl)-4-hydroxyphenyl]methane and di(hydroxymethyl)urea polycondensation products are formed as side products. By varying the reaction conditions, namely the temperature (50–100 °C), the di(hydroxymethyl)urea : DTBP molar ratio (1 : 2.5–10), and the catalyst (HCOOH, KU-2 resin, HCl, sulphopolyphenyl ketone), the yield of substituted urea was raised only to 24%. The replacement of di(hydroxymethyl)urea by its dimethyl ether in this reaction (in order to prevent polycondensation) resulted in only a slight improvement of the yield of the required product—to 31%.

Table 2. Synthesis of substituted ureas by the catalytic carbonylation of amines.[164]

Amine	Catalyst	T, °C	Yield, %
Diethylamine	NiI_2	280	72
Butylamine	NiI_2	200	40–45
Ditto	$Mn_2(CO)_{10}$	180–200	47
Cyclohexylamine	$Mn_2(CO)_{10}$	180–200	58
Hexamethyleneamine	Co	200	—
Aniline	Co	200	75
Ditto	$Mn_2(CO)_{10}$	190	6
"	NiI_2	160	26
" *	Pd, Pd/C, $PdCl_2$	180	—
" **	Te	140	—

*See Tsuji and Iwamoto.[156]
**See Kambe et al.[165]

6. The Synthesis of Substituted Ureas by the Carbonylation of Amines

(a) Catalytic carbonylation of amines. Substituted ureas can be obtained by the catalytic carbonylation of amines,[156–162] using transition metals and their salts and carbonyls as catalysts (Table 2). The reaction is performed at 150–280 °C and a carbon monoxide pressure of 100–300 atm. Its products are *N*-formylureas and other substituted urea derivatives. This method has significant advantages over the method involving the treatment of amines by phosgene, used at present in industry, since it makes it possible to avoid the use of a poisonous component (phosgene) and in addition the carbonylation of amines results in the formation of hydrogen[156] and water[159–161] together with the required products and not hydrochloric acid as in the reaction with phosgene. The catalytic carbonylation of amines yields substituted ureas in a single stage under mild conditions.[163]

The large set of chemical substances of different kinds tested as catalysts shows that a purely empirical approach has been used. This is because the amine carbonylation process has been inadequately investigated.

Numerous mechanisms have been proposed for this reaction. They are as a rule contradictory and have not been confirmed by kinetic data. Thus it has been shown[166–168] that amines react with transition metal compounds to form charge-transfer complexes, which, on heating and on treatment with oxidants, are capable of undergoing deprotonation and homolytic decomposition with formation of the aminyl radical and a change in the oxidation state of the complex-forming agent. A chain reaction mechanism has been proposed in which the metal salts serve as the sources of radicals at the instant of reaction.[166] It has been suggested[169] that, in the presence of I_2 and $KMnO_4$, the reaction proceeds in accordance with an analogous mechanism.

Another carbonylation mechanism has been discussed by Dombek and Angelici,[170] who believe that $Fe(CO)_5$ reacts with the amine to form a carbamoyl complex, which is of key importance in the catalytic process. The reaction with $Mn_2(CO)_{10}$ [162] and certain other transition metal compounds, which are reduced to the metal under the reaction conditions (100–200 °C, 100 atm CO) and are capable of forming carbonyls, apparently proceeds analogously. The reaction results in the formation of either formamides or, when NiI_2, Co, or $Mn_2(CO)_{10}$ are used as catalysts, a mixture of formamides and substituted ureas; the latter are formed preferentially in the presence of $Mn_2(CO)_{10}$.

The composition of the products depends significantly on the nature of the amine. Thus it has been shown[156] that the carbonylation of lower aliphatic amines gives rise to only a small amount of ureas together with formamides, while aromatic amines produce only ureas.

It has been suggested[171,172] that ureas are formed in two stages via an intermediate formamide:

$$RNH_2 + CO \rightarrow RNHCOH \ ;$$

$$RNHCOH + H_2NR \rightarrow (RNH_2)_2CO \ .$$

Analysis of the views expressed in the literature on the mechanism of the amine carbonylation reaction shows that they require careful checks and investigation. Thus essentially the same mechanism has been proposed[158,166] for severe and mild conditions, although the reaction products are completely different. The high selectivity of the reaction as regards the formation of formamides under severe conditions and of urea under mild conditions is incompatible with a radical mechanism.

(b) Oxidative carbonylation of amines. In the amine carbonylation reactions examined above the catalyst either does not undergo a change in valence or is reduced with transfer of one electron. An interesting method of synthesis of substituted ureas involves the oxidative carbonylation of amines, which takes place on reduction of the metal complex (transfer of two electrons) or in a catalytic process in the presence of an additional oxidant. Apart from metal complexes, the reaction is catalysed by elemental sulphur and selenium. The oxidative carbonylation of amines is carried out under mild conditions, which is of practical interest.

Substituted ureas have been obtained in high yields by the reaction[173–175]

$$CO + S + RNH_2 \rightarrow RNHCONHR + H_2S \ .$$

The reaction involving aromatic amines takes place under mild conditions (100–160 °C, 20–40 atm), while that of aliphatic amines requires more severe conditions. The yield of ureas increases on raising the temperature and when a solvent (ethanol) is employed.

When selenium is used instead of sulphur, the reaction conditions become much milder (20 °C, 1 atm CO).[176] The yield of substituted ureas formed from primary amines is 95–99%, but that formed from secondary amines is much lower. Seleno-carbamates have been isolated as intermediates. It has been shown that the active carbonylating agent is selenium carbonyl.[177,178] An excess of oxygen in the CO + O_2 mixture leads to the precipitation of elemental selenium and the cessation of the catalytic reaction. It is believed[176] that the reaction takes place in at least two stages:

$$RNH_2 + Se + CO \rightarrow (RNH_3)^+ (RNHC(=O)Se)^- \ ;$$

$$(RNH_3)^+ (RNHC(=O)Se)^- + O_2 \rightarrow (RNH_2)_2CO + H_2O + Se \ .$$

Carbonylation of primary amines in the presence of silver acetate under mild conditions (0–25 °C, 55–100 atm) afforded *NN*-dialkylureas in almost quantitative yields.[157] Copper, zinc, cadmium, cobalt, and nickel acetates are inactive, while $Pd(Ac)_2$ is weakly active.

In the presence of $CuCl_2$, substituted ureas are obtained at room temperature and atmospheric pressure of CO:[179,180]

$$R^1R^2NH + CO + Cu^{II} \rightarrow R^1R^2NCONR^1R^2 + H_2O + Cu^I .$$

Since univalent copper complexes are readily reoxidised by oxygen, the overall reaction has the following form:

$$R^1R^2NH + CO + O_2 \xrightarrow{Cu^{I,II}} R^1R^2NCONR^1R^2 + H_2O .$$

The reaction can be performed in many solvents and in their absence. Piperidine and morpholine show the highest reactivity, while diethylamine, pyrrolidine, cyclohexylamine, and butylamine are less reactive.

It has been found[158] that, in the temperature range 25–110 °C at atmospheric pressure, the carbonylation of certain primary and secondary amines in the presence of $PdCl_2$ and $Hg(CH_3COO)_2$ is a stoichiometric oxidation-reduction reaction, which takes place in four stages:

(1) the formation from the amine and the metal salt of a compound having the character of a charge-transfer complex:

$$R_2NH + Hg(CH_3COO)_2 \rightarrow (R_2NH)_2Hg(CH_3COO)_2 .$$

(2) The interaction of the complex formed with CO accompanied by the insertion of the latter in the metal–nitrogen bond:

$$(R_2NH)_2Hg(CH_3COO)_2 + CO \rightarrow R_2NCHg(CH_3COO) + R_2NH \cdot CH_3COOH .$$

(3) The redox decomposition of the carbamoyl complex with formation of active radical species and the reduction of the metal ion:

$$R_2NCHg(CH_3COO) \rightarrow R_2NC\cdot + Hg(CH_3COO) .$$

(4) The recombination of the active species to the reaction products:

$$2R_2NC\cdot \rightarrow R_2NC{-}CNR_2 \xrightarrow{\Delta} R_2NCNH_2 + CO .$$

In a complex system comprising organic phosphines, quaternary ammonium bases, and tetraethylammonium chloride, palladium complexes effect the catalytic carbonylation of amines to *NN'*-disubstituted ureas in the presence of nitro-compounds as oxidants at 90 °C and a CO pressure of 1 atm.[181]

The synthesis of substituted ureas by the oxidative carbonylation of n-butylamine and piperidine in the presence of palladium(II) complexes, copper(I, II) complexes, or the highly active catalytic system comprising both copper(II) and palladium(II) complexes has been investigated.[163] The last catalytic system retains its activity in reactions with different amines in a number of solvents (dioxan, ethanol, pyridine, and acetonitrile). It has been established[163] that, in the presence of palladium complexes, the reaction proceeds via the formation of a carbonyl complex, which is subsequently converted, as a result of nucleophilic attack by the amine on the coordinated carbon monoxide, into a carbamoyl intermediate, whose redox decomposition is the rate-limiting stage of the process. The amine-copper(II) complexes greatly accelerate this decomposition. When bivalent palladium and copper complexes are used, a synergistic effect is observed.

Thus the oxidative carbonylation of amines is an effective and promising method of synthesis of substituted ureas. However, this reaction has so far been inadequately investigated. The studies which have been made are in the main preparative and the reaction mechanism has been scarcely investigated.

Symmetrical dialkyl- or diaryl-ureas have been obtained in 50–90% yields by condensing the corresponding amine with carbon dioxide at 100–300 °C and a pressure of 100–300 atm.[182–187]

7. Synthesis of Substituted Ureas and Acid Amides (Hofmann Rearrangement)

Hofmann found in 1881 that the reaction of amides with bromine in the presence of alkali results in the formation of 1,3-alkylacylureas, which are converted into alkylureas on subsequent treatment with nitric acid:[188,189]

$$CH_3CONH_2 \xrightarrow[-HBr,\ -H_2O]{NaOH+Br_2} CH_3CONa \xrightarrow[-NaNO_3,\ -HBr]{HNO_2} CH_3NCO \rightarrow$$
$$\rightarrow CH_3NHCONHCOCH_3 \xrightarrow[-CH_3COOH]{H_2O} CH_3NHCONH_2 .$$

The corresponding *NN*-dialkyl-*N'*-arylureas have been obtained in 20–60% yields from aromatic acid amides and secondary amines in the presence of potassium hypochlorite.[190]

III. APPLICATIONS OF SUBSTITUTED UREAS

Substituted ureas, which constitute some of the most important classes of chemical compounds, have found extensive applications in agriculture as plant growth regulators and pesticides, particularly herbicides. This question has been widely dealt with in the literature. A systematic account and a survey of data on the effectiveness of ureas as plant growth regulators and herbicides have been given in a review,[191] in which certain regularities in the herbicidal activity of substituted ureas as a function of their structure have been established. A bibiographic index of recommended pesticides and plant growth regulators, covering the literature up to 1979, has been published;[192] much space in it has been devoted to substituted ureas.

Studies in this field are developing vigorously; new communications on the efficiency of substituted ureas as herbicides,[12–14,17–19,36,38,41,42,193–210] and plant growth stimulators,[38,211–213] as well as fungicides,[17,19,22,205,213–215] insecticides,[23,24,37,39,216–218] bactericides,[60,213,219] and other pesticides,[16,34,220] promising for practical applications, are being published systematically.

Yet another field in which substituted ureas are widely employed is that of the manufacture of physiologically active substances[34,221–225] and medicinal preparations, mainly with tranquillising and anticonvulsant activities.[226–231] Various *N*-alkyl-*N'*-aminophenoxyureas are used in the treatment of asthma and other diseases of the respiratory tract[59,232] and substituted ureas are used as components of medicinal preparations for the treatment of cardiac diseases.[233]

Certain nitroureas exhibit anticancer and antileukaemic properties,[54,234–242] heterylcarbonylureas dissolve gall stones,[243] while indolylureas, amidinoureas, *N*-aryl-*N'*-imidazolidineureas, aminoethylureas, and piperidinylureas possess hypotensive properties.[58,244–248]

Sulphonylureas and 1-amidino-3-phenylureas exhibit dermatological properties.[249,250] The latter can also be used to reduce blood pressure[245] and in the treatment of

increased acidity and stomach ulcers;[251,252] *N*-alkyl-*N'*-dialkylaminoethylureas[253] and pyrazinylureas can also be employed in the treatment of gastrointestinal diseases;[254] certain substituted ureas are used as agents for the protection of the skin against boils.[255]

Certain phenylureas are capable of inhibiting the degradation of connective tissues in warm blooded animals and in man.[256] Ureas with nitrogen-containing heterocycles can be used as regulators of immune responses,[28] as antihelminthic preparations,[26,257] and as hypoglycaemic substances.[258,259]

Data concerning the use of substituted ureas for the dyeing of hair and keratin and cellulose fibres have been described in the literature;[260,261] 3-hydroxy-2,4-dimethylphenylurea is the most effective.[103,262] Substituted ureas are able to form complexes with certain metal ions and they are used in analytical chemistry as complex forming agents.[263,268] Certain urea derivatives (for example, the symmetrical diethylphenylurea under the name centramit) serve as stabilisers of smokeless powders;[152] 1,3-dialkylureas are used in the synthesis of sweetening agents and as sugar substitutes.[269]

Tetramethylurea is used as a solvent in polarography.[270] Urea derivatives are also employed as solvents for quinone or hydroquinone in the manufacture of hydrogen peroxide[271] and as solvents and catalysts in chlorination reactions.[164]

Substituted ureas can serve as the starting materials for the synthesis of polymers[61,221,222,272-276] and also surfactants.[277]

Substituted ureas have assumed special importance recently as effective additives to hydrocarbonfuel oils and polymeric materials. They have been studied in detail as antioxidants in various types of petrol for automobiles.[32,33,278-280] Thus the study of various derivatives of *p*-hydroxyphenylurea showed[278-280] that the substitution of hydrogen at the nitrogen atom by various aliphatic and aromatic groups leads to the appearance of an appreciable antioxidant effect, while *p*-hydroxyphenylurea itself does not inhibit the oxidative processes in petrols. *N*-Alkyl-*N'*-(*p*-hydroxyphenyl)ureas, *N*-(4-hydroxy-3-methylphenyl)-*N'*-phenylurea, and *N*-butyl-*N*-phenyl-*N'*-(*p*-hydroxyphenyl)urea, used at a concentration of 0.06%, exhibit the highest effectiveness.

The influence of *N*-(*p*-hydroxyphenyl)-*N'*-pentylurea and *NN'*-dipentylurea on the thermo-oxidative stability of TS-1 and T-2 reactive fuels has been investigated.[281] In contrast to their effect on petrols,[55] in reactive fuels the test compounds proved to be relatively ineffective; in their presence the decrease in deposit formation was only by 20–30% (the concentration of the additive was 0.05 wt.%).

The study of the influence of various alkyl- and alkylaryl-ureas on the thermo-oxidative stability of straight-run reactive fuels of the T-1 type showed that *N*-alkyl and *NN*-dialkylureas are the most effective and reduce deposit formation in the fuel by 80–90%.[141,282] It has been established that substituted ureas which effectively reduce deposit formation in the fuel have almost no influence on the oxygen absorption process; this apparently shows that the anti-deposit formation function of the test compound is not associated with the antioxidant activity and is due to a dispersing type of activity. Compounds in which a urea fragment, with its dispersing activity, and a typical antioxidant fragment, namely 2,6-di(t-butyl)phenol, are combined in one molecule are effective stabilisers of reactive fuels.[156,283-285] Certain *N'*-acylaminoacyl derivatives of *N*-substituted ureas are also highly effective in stabilising reactive fuels obtained by hydrogenation processes.[286]

Kuliev and co-workers[152-154] proposed *NN'*-di(alkylbenzyl)-ureas as antioxidant additives to energy oils. For example, the additive obtained by condensing a mixture of C_8–C_{12} alkylphenols with urea and formaldehyde (AZNII-11) has antioxidant properties in oils which are not inferior to those of antioxidants such as ionol and *p*-hydroxydiphenylamine.

Apart from antioxidant properties, some of the substituted ureas behave as corrosion inhibitors when added to fuels and oils.[287-288] Thus *N*-alkyl-*NN'*-di(carboxymethyl)ureas containing 15–45 carbon atoms, preferably with an unbranched hydrocarbon chain, for example *N'N'*-di(carboxymethyl)-*N*-octadecylurea $C_{18}H_{37}NHCON(CH_2COOH)_2$ have been proposed as effective corrosion inhibitors in light distillate fuels.[287]

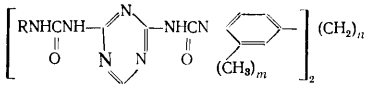
The alkenylsuccinimide based on urea (SIM), obtained by aminating alkenylsuccinic anhydride with urea, is used as a corrosion inhibitor in engine conservation oils for different purposes.[288,289] Its use ensures a high protective capacity and effective operating properties of the oils.

In many instances substituted ureas are used as detergent additives and additives preventing the formation of carbon deposits.[290,291] Monosubstituted ureas with an overall number of carbon atoms between 5 and 25 are used to remove carbon, varnish, and other deposits formed in the injection system of an internal combustion engine. Octadecyl-, dodecyl-, and 9-octadecynyl-ureas are the most effective (they are recommended for use in hydrocarbon fuels with a boiling range of 38–400 °C).

A reduction of the extent of deposition in the carburettor of an internal combustion engine is achieved by introducing into petrol additives which are products of the interaction of air-oxidised liquid paraffin and a substituted urea having the general formula $RNH(CH_2)_xNHCONH(CH_2)_xNHR'$, where $x = 2$–4 and R and R' are saturated secondary aliphatic C_{10}–C_{15} groups.[291]

Some investigors have successfully solved the problem of reducing the setting temperatures of diesel fuels with the aid of substituted ureas.[292,293] Compounds have the general formula $\begin{matrix}R_1\\R_2\end{matrix}\!\!>\!NCONH_2$ ($R^1 = C_3$–C_{20} alkyl groups, R^2 = phenyl), particularly *N*-phenyl-*N*-propylurea, produced a satisfactory result.[292] Alkylisoureas RNHCOR, where R = $\begin{matrix}\\\|\\NH\end{matrix}$ C_{16}–C_{20} alkyl groups, have also proved to be more effective depressors of the setting temperatures of diesel fuels.[293]

Compounds of urea and triazine having the general formula



where R = C_{16}–C_{22} aliphatic group and *m* and *n* = 0 or 1 have been proposed as thickening additives to high-temperature plastic lubricants,[40] while halogenoarylureas are effective hardening agents for epoxy resins.[294-296]

It has been suggested that benzylureas be used as antioxidants for certain polymers.[297] It has been established that 3-alkylbenzyl-1-phenylurea at a concentration of 0.1% is the most effective in tests in polypropylene.

An important problem which has been solved successfully with the aid of substituted ureas is that of the prevention of the cracking of rubbers under the influence of ozone.[298-300] Substituted ureas having the general formulae ArNHCONHAr' (Ar and Ar' are various aromatic groups), for example, *N*-naphthyl-*N'*-*p*-tolylurea,[298] and $R^1R^2NCONR^3R^4$ (R^1, R^2, R^3, and R^4 are hydrogen or hydrocarbon groups, two of which are alicyclic) have been proposed.[209] For example, *NN*-dicyclohexyl-*N'*-phenylurea at a concentration of 1.5% reacts with butadiene–styrene raw rubber to form a vulcanised rubber which hardly cracks under the influence

of ozone. Substituted ureas with the above structure do not dye or decolorise the raw material to which they are added.

Urea derivatives have been proposed as anti-ageing agents[301] and thermal stabilisers[302] for synthetic rubbers. Diphenylurea prevents the cross-linking of synthetic rubbers to a high degree of unsaturation.[303] It has also been stated that urea derivatives with aromatic and aliphatic acyl groups can function as thermal stabilisers not only for rubbers but also for plastics and oils,[304] while dihydroxyalkylureas can be used as modifying agents (chain lengthening agents) for urethane thermoelastoplastics.[305]

Derivatives containing urea residues have been patented as stabilisers preventing changes in the mechanical properties and colour of polyurethane resins, foam plastics, fibres, synthetic leather, and elastomers under the influence of sunlight, ultraviolet irradiation, or heat.[306]

It has been suggested that substituted ureas be used as stabilisers for higher ketone peroxides (vulcanising agents for polyester resins)[307] and as stabilisers preventing the formation of a sludge from hydrocarbons, lubricating materials, and fuels.[308]

Substituted ureas are used for the bleaching[309] of fabrics and for imparting hydrophobic properties to the latter,[310] for the impregnation[311] of synthetic fibres, and for the improvement of their formation.[312]

Data have appeared recently in the literature[313] demonstrating the possibility of using substituted ureas as additives imparting fire resistance to synthetic fibres. For example, for this purpose polyamide fibres have been impregnated with a solution containing urea or some of its derivatives, such as *NN*-diphenylurea, *N*-α-naphthylurea, and *NN*-dimethyl-*N'*-phenylurea.[313] *N*-Substituted derivatives of ethyleneurea can be used as ink stabilisers.[314] Inks containing substituted ureas are highly stable during use and storage and possess satisfactory physical properties.

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Analysis of the literature data on the methods of synthesis of substituted ureas demonstrates their wide variety, but many of them suffer from various disadvantages which limit their application. Thus the amide method is characterised by low yields and the use of isocyanates for synthesis is difficult because they are not readily available, the condensation of hydroxymethylurea with phenols is accompanied by the formation of a large number of side products, while treatment of amines with phosgene makes it possible to obtain substituted ureas in high yields but the high toxicity of phosgene makes it difficult to work with this substance. From the standpoint of the ready availability of the starting material and simplicity, the interaction of urea or nitrourea with amines constitutes a convenient method of synthesis of substituted ureas but even this procedure suffers from certain limitations, because, depending on the amine employed, it gives rise to mono- or *NN*-disubstituted ureas. All these disadvantages and limitations must be taken into account in selecting the methods for the synthesis of particular urea derivatives.

The literature data which have been published recently show that, together with the traditional applications of substituted ureas (pesticides, medicinal preparations, and dyes), these compounds are highly effective as modifying and stabilising agents for various organic materials. One of the aims of the review is to draw the attention of investigators, working in the field concerned with the improvement of the quality of polymers and petroleum products with the aid of additives, to this promising class of compounds.

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Furo-, Thieno-, and Pyrrolo-[2,3-*d*] Pyrimidines

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The methods of synthesis and the chemical and biological properties of furo-, thieno-, and pyrrolo-[2,3-*d*] pyrimidines are described.
The bibliography includes 201 references

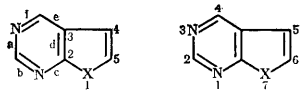
CONTENTS

I. Introduction 262
II. Methods of synthesis 262
III. Chemical reactions 268
IV. Biological properties 272

I. INTRODUCTION

Furo-, thieno-, and pyrrolo][2,3-*d*]pyrimidine derivatives occupy an important place among various heteroatomic bicyclic systems because they include compounds with different types of biological activity. Furthermore, these bicyclic compounds represent to a greater or lesser extent the structural analogues of biogenic purines and from this standpoint can be regarded as potential antimetabolites in nucleic acid metabolism. These data have served and continue to serve as a basis for the synthesis of a wide variety of derivatives of furo-, thieno-, and pyrrolo-[2,3-*d*]pyrimidines in order to discover physiologically active substances among them.

The IUPAC nomenclature and the numbering for these bicyclic systems, which we shall henceforth employ in the present review, are given below.



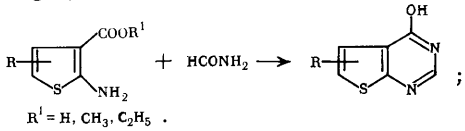
X = O, S, NH

Although the first communication on the synthesis of pyrrolo[2,3-*d*]pyrimidine appeared as early as 1911,[1] systematic studies on furo-, thieno-, and pyrrolo-[2,3-*d*]pyrimidines were begun 20–25 years ago. The methods of synthesis of these compounds can be divided into two groups: from derivatives of a five-membered heterocycle (furan, thiophen, and pyrrole) and from derivatives of a six-membered heterocycle (pyrimidine, oxazole, and thiazole).

II. METHODS OF SYNTHESIS

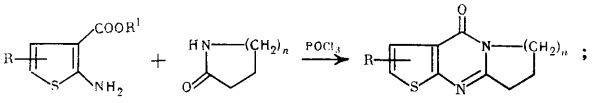
1. Methods of Synthesis from a Five-membered Heterocycle

Derivatives of 2-aminofurans, 2-aminothiophens, and 2-aminopyrroles containing the carbonyl or cyano-group in the 3-position in the five-membered ring have been widely used as the starting compounds for the synthesis of the bicyclic derivatives under consideration. Thus, when 2-aminothiophen-3-carboxylic acid or its esters are heated with formamide, 4-hydroxythieno[2,3-*d*]pyrimidines are formed in high yields:[2-8]



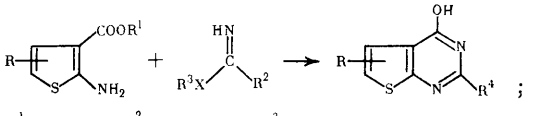
R^1 = H, CH_3, C_2H_5 .

Other workers[9] used the corresponding lactams instead of formamide; the yield of thienopyrimidine was 40–90%:



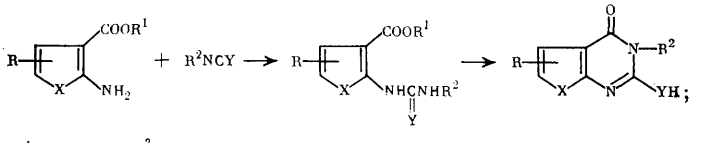
R^1 = H, C_2H_5; n = 1, 2, 3 .

The esters of 2-aminothiophen-3-carboxylic acid react with urea,[6,10] thiourea,[11] and iminoesters[11,13] to form the corresponding 2-substituted 4-hydroxythieno[2,3-*d*]pyrimidines:



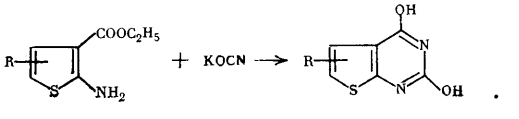
R^1 = CH_3, C_2H_5; R^2 = NH_2, Alk, Ar; R^3 = H, C_2H_5; R^4 = OH, SH, Alk, Ar; X = O, S .

The reactions of 2-amino-3-ethoxycarbonylthiophen with isocyanates,[14,15] isothiocyanates[11,16-25] and isoselenocyanates[26] lead to the formation of intermediate 3-ethoxycarbonyl-2-thienylureas (and the corresponding thioureas and selenoureas), which cyclise in an alkaline medium to the corresponding 2-substituted 3-alkyl(aryl)-4-hydroxythieno-[2,3-*d*] pyrimidines. An analogous reaction with isocyanate is known for 2-amino-3-methoxycarbonylfuran[27] and the corresponding pyrrole:[28]

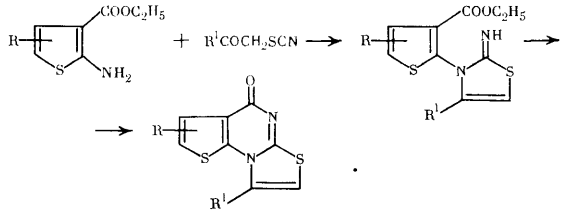


R^1 = CH_3, C_2H_5; R^2 = Alk, Ar; X = O, S, NH; Y = O, S, Se .

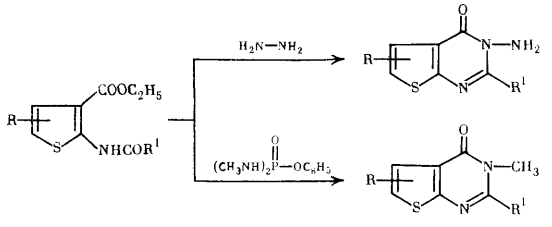
In an aqueous solution of potassium cyanate 2-amino-3-ethoxycarbonylthiophen cyclises 2,4-dihydroxythieno-pyrimidine in 70% yield:[29]



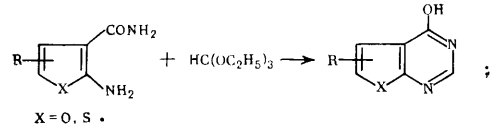
There is an interesting reaction between 2-amino-3-ethoxycarbonylthiophen and α-thiocyanatoacetone[30] or the corresponding acetophenone,[31] which results in the formation of the bicyclic thiazolothienopyrimidine system:



The interaction of 2-acylamino-3-ethoxycarbonylthiophen with hydrazine hydrate[32] or phenyl *NN*-dimethylphosphorodiamidate[33] results in the formation of 2-alkyl-3-amino- or 2-alkyl-3-methyl-4-oxo-thieno[2,3-*d*]pyrimidines respectively:

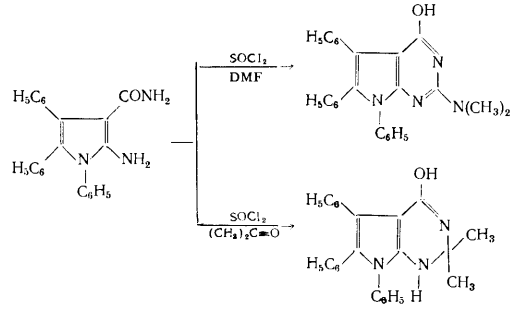


The 3-carbamoyl derivatives of the five-membered heterocycles can also participate in the cyclisation reactions. Thus 2-amino-3-carbamoylfurans[34,35] and the corresponding thiophens[5] react with orthoformic ester or with the acid itself[6] to form the corresponding 4-hydroxy-derivatives:

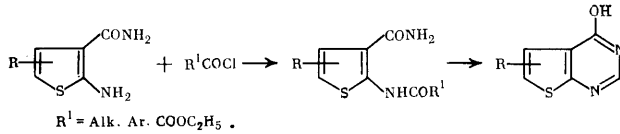


X = O, S.

On treatment with thionyl chloride in dimethylformamide (DMF), 2-amino-3-carbamoyl-1,4,5-triphenylpyrrole cyclises to 4-hydroxy-2-dimethylaminopyrrolo[2,3-*d*]pyridimine, while in acetone it cyclises to 2,2-dihydro-4-hydroxy-2,2-dimethylpyrrolopyrimidine:[36]

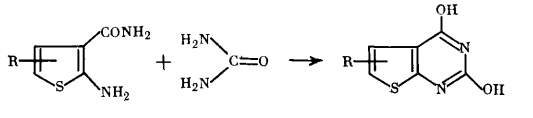


2,3-Substituted 4-hydroxythienopyrimidines can be synthesised from 2-acylamino-3-carbamoylthiophens:[6,37-39]

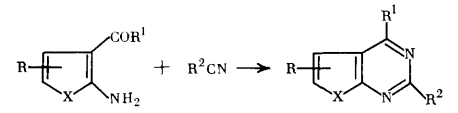


R^1 = Alk, Ar, $COOC_2H_5$.

When 2-amino-3-carbamoylthiophen is heated with urea, 2,4-dihydroxythieno[2,3-*d*]pyrimidine is formed in 40% yield:[6]

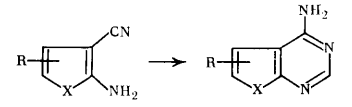


2-Amino-2-carbamoyl-, 2-amino-3-ethoxycarbonyl, and 2-amino-3-benzoyl-furans and the corresponding thiophens and pyrroles react with various nitriles to form the corresponding bicyclic compounds in 50–85% yields:[40]



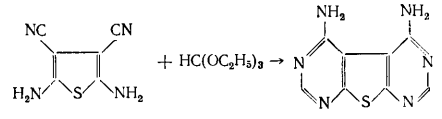
X = O, S, NH; R^1 = NH_2, $NHCH_3$, OC_2H_5, C_6H_5; R^2 = Alk, Ar.

When 2-amino-3-cyanofurans and the corresponding thiophens or pyrroles are used in the syntheses, it is possible to obtain systems containing the amino-group at the C(4) atom of the pyrimidine ring. Thus the corresponding 4-amino-derivatives have been obtained by heating 2-amino-3-cyanofuran and the corresponding thiophen or pyrrole with formamide,[41-44] orthoformic ester in the presence of ammonia,[45-49] or formamidine acetate:[50,51]

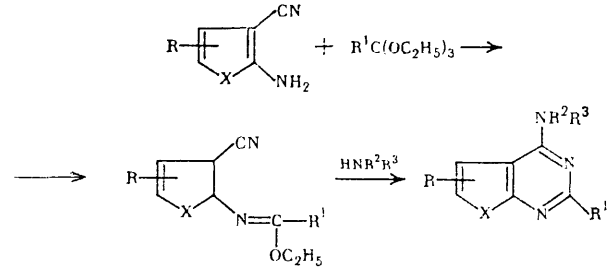


X = O, S, NH.

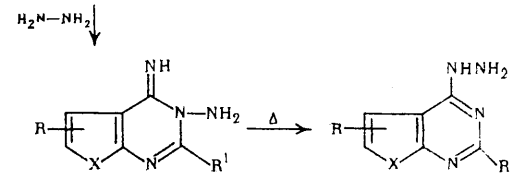
2,5-Diamino-3,4-dicyanothiophen reacts with orthoformic ester in the presence of ammonia and cyclises to 4,4'-diaminothieno[2,3-*d*;2',3'-*d*]dipyrimidine:[48]



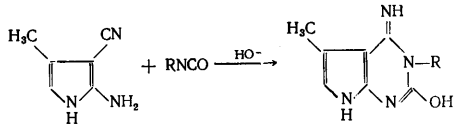
The first stage of the reaction of the corresponding furan or thiophen with orthoformic ester in the presence of ammonia usually involves the formation of 2-alkoxyethyleneimino-3-cyanofuran(or thiophen), which can be made to react with hydrazine[52] or substituted amines[53-56] to form the corresponding 4-amino-derivatives:



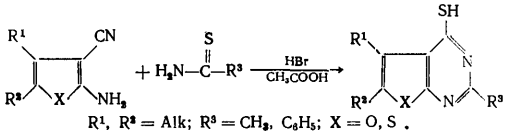
X = O, S; R^1 = H, Alk; R^2, R^3 = H, Alk, Ar;



2-Amino-3-cyanopyrrole cyclises on treatment with isocyanates in an alkaline medium to 3-alkyl-4-amino-2-oxopyrrolo[2,3-*d*]pyrimidine:[28]

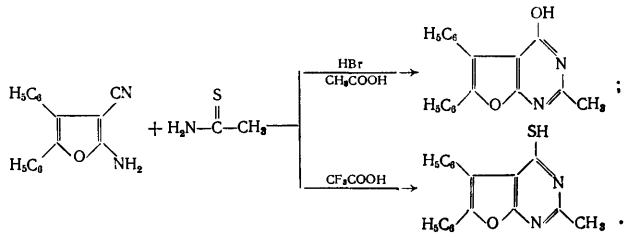


A study of the reaction of 2-amino-3-cyanofurans and the corresponding thiophens with thioamides established that the 4,5-dialkyl derivatives of these heterocycles in an acid medium give rise to 2-mercaptofuro- and 4-mercaptothienopyrimidines:[57]

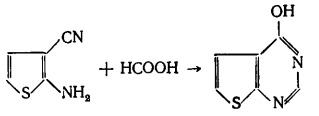


R^1, R^2 = Alk; R^3 = CH_3, C_6H_5; X = O, S .

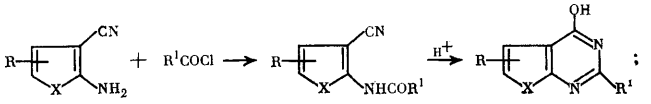
Under the conditions indicated above, 2-amino-3-cyano-4,5-diphenylfuran reacts with thioacetamide to form 4-hydroxyfuropyrimidine, while in the presence of trifluoroacetic acid it cyclises to 4-mercaptofuropyrimidine:



It is noteworthy that, on treatment with formic acid in the presence of sodium acetate, 2-amino-3-cyanothiophen also cyclises to 4-hydroxythieno[2,3-*d*]pyrimidine:[6]

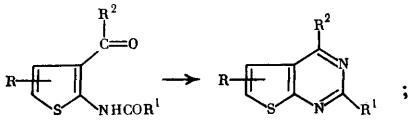


In an acid medium 2-acylamino-3-cyanofuran and the corresponding thiophens give rise to the corresponding 4-hydroxy-derivatives:[57]



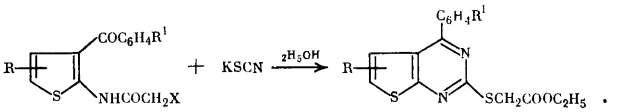
X = O, S; R^1 = CH_3 C_6H_5 .

2-Aminothiophen-3-carbaldehydes and the corresponding ketones have found an application in the syntheses of thieno-[2,3-*d*]pyrimidines. In the presence of ammonium acetate, ammonia, or formamide they cyclise to 2,4-dialkyl(aryl)thienopyrimidines:[6,58–62]

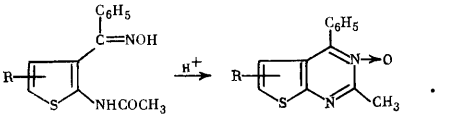


R^1 = Alk, Ar; R^2 = H, C_6H_5 .

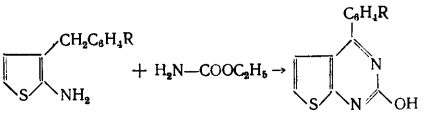
The reaction of 3-benzoyl-2-α-halogenoacylaminothiophen with potassium thiocyanate leads to the formation of 2-alkylthio-4-phenylthieno[2,3-*d*]pyrimidine:[63]



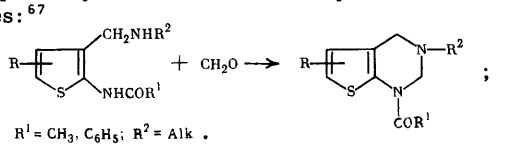
The oximes of 2-acylamino-3-benzoylthiophens cyclise in an acid medium to the corresponding *N*-oxides:[64,65]



In conclusion one may quote non-standard reactions whereby thiophens and pyrroles can be converted into thieno- and pyrrolo-pyrimidines. Thus 2-hydroxy-4-phenylthienopyrimidines have been obtained by heating 2-amino-3-benzylthiophen with urethane:[66]

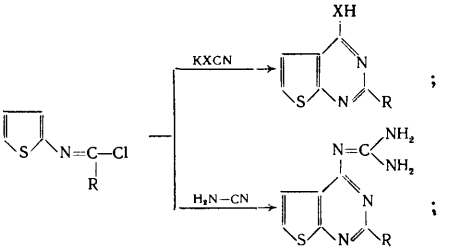


On treatment with formaldehyde, 2-acylamino-3-aminomethylthiophens cyclise to 1,2,3,4-tetrahydrothieno[2,3-*d*]-pyrimidines:[67]



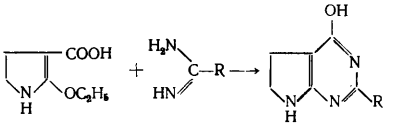
R^1 = CH_3, C_6H_5; R^2 = Alk .

The study of the reaction of *N*-(2-thienyl)chloroformamidines with isocyanates and cyanamide led to the synthesis of a series of 2-amino-4-substituted thienopyrimidines:[68]



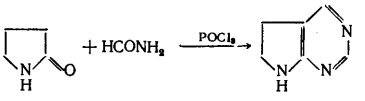
X=O, S, Se; R=N(CH_3)$_4$, N(CH_2)$_5$, N(CH_2CH_2)$_2$O .

3-Carboxy-2-ethoxy-4,5-dihydropyrrole reacts with urea, thiourea, or acetamidine to form the corresponding pyrrolopyrimidines, the yield of the product varying in the range from 5 to 70% depending on the character of the reactant:[69,70]

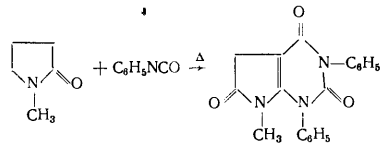


R=OH(4%); H(71%); SCH_3(5%), NH_2(59%); CH_3(40%) .

On treatment with formamide in the presence of phosphoryl chloride, 2-pyrrolidinone is converted into 5,6-dihydropyrrolo[2,3-*d*]pyrimidine:[71]

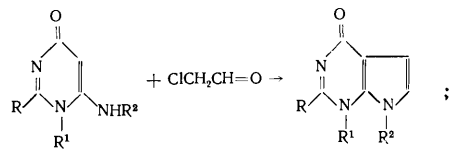


When 1-methyl-2-pyrrolidone is heated with phenyl isocyanate, 5,6-dihydropyrrolopyrimidine is formed:[72]



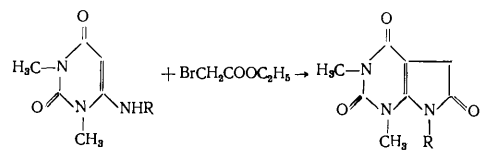
2. Methods of Synthesis from Six-membered Heterocycles

In this synthetic procedure, either pyrimidines without substituents at the C(5) atom but with different functional groups (hydroxy-, mercapto, and amino-groups) at the C(2), C(4), and C(6) atoms of the pyrimidine ring or the corresponding 5-substituted 6-hydroxy-, 6-amino-, and 6-mercapto-pyrimidines are usually employed. In the first case α-halogenocarbonyl compounds are used as the second component and the reaction with these substances can proceed both via the C(5) atom of the pyrimidine ring and via the 6-hydroxy-, 6-mercapto-, or 6-amino-group. Thus 2-substituted 6-amino-4-hydroxypyrimidines react with chloroacetaldehyde to form the corresponding pyrrolopyrimidines:[73-75]

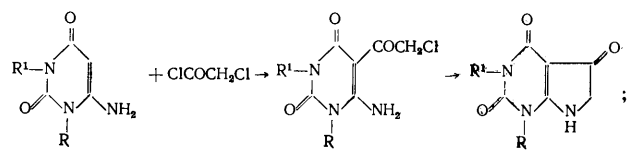


R=OH, SH, SCH_3, NH_2; R^1=H, CH_3; R^2=H, Alk.

On treatment with bromoacetic ester, 6-amino-1,3-dimethyluracil cyclises to 2,4,6-trioxopyrrolopyrimidine:[76]

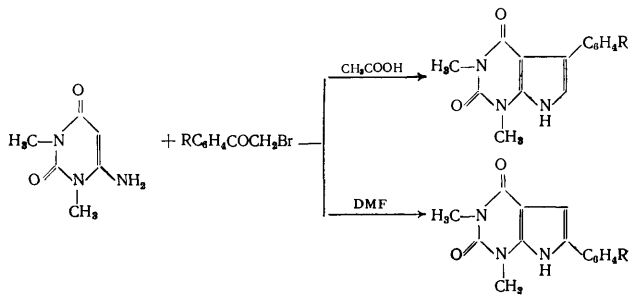


Chloroacetyl chloride also reacts with 6-aminouracils to form 5-acyl derivatives, which cyclise to 2,4,5-trioxopyrrolopyrimidines:[75,77]



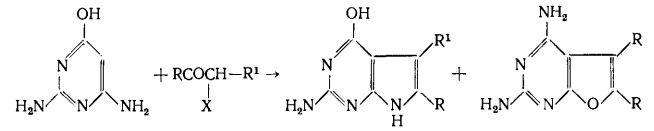
R=H, CH_3, C_2H_5, C_6H_5; R^1=H, CH_3.

Japanese workers[76,78] have shown that 6-amino-1,3-dimethyluracil reacts with phenacyl bromides via two different pathways depending on the conditions. 5-Phenyl- and 6-phenyl-pyrrolo[2,3-*d*]pyrimidines are formed in the presence of acetic acid and in DMF respectively:



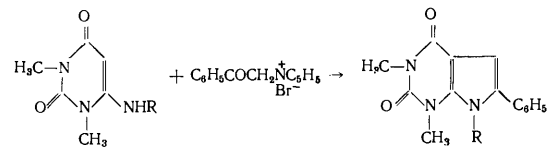
Evidently in the former case a molecule of hydrogen bromide is split off by reaction with the amino-group and in the latter case by reaction with the C(5)–H bond in the pyrimidine ring.

In the interaction of 2,4-diamino-6-hydroxypyrimidine with α-halogenoketones there is a possibility of the formation of both pyrrolo- and furo-[2,3-*d*]pyrimidines. Indeed, depending on the character of the ketone, either a mixture of these compounds or only one of the possible products is formed:[79]

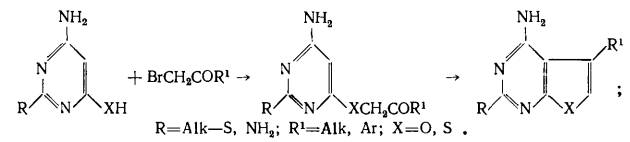


X=Cl, Br; R=H, C_6H_5, Alk; R^1=H, CH_3.

Instead of the α-halogenocarbonyl compounds, the corresponding pyridinium salts are sometimes employed. Thus 6-amino-1,3-dimethyluracil reacts with phenacylpyridinium bromide to form 6-phenylpyrrolopyrimidine:[80]

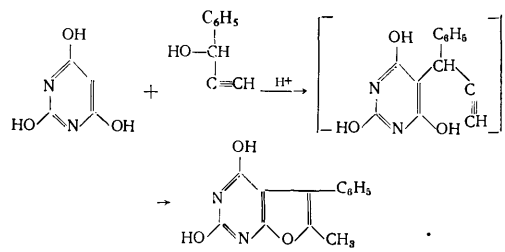


Certain 6-hydroxy- and 6-mercapto-pyrimidines can be alkylated at the hydroxy- and mercapto-groups with subsequent cyclisation to the corresponding furo-[81] or thieno-pyrimidine:[82,83]

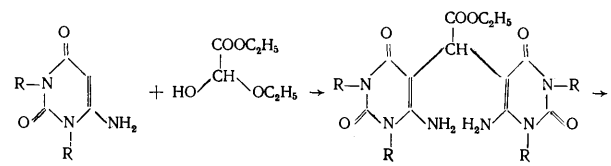


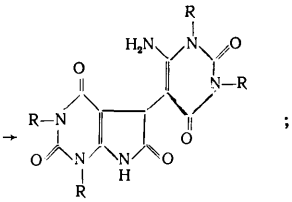
R=Alk—S, NH_2; R^1=Alk, Ar; X=O, S.

Instances of the employment of reactive hydroxy-compounds in the syntheses of furo- and pyrrolo-pyrimidines are known. Thus, when α-phenylpropargyl alcohol is heated with barbituric acid in the presence of sulphuric acid or boron trifluoride, 2,4-dihydroxy-6-methyl-5-phenylfuro[2,3-*d*]pyrimidine is formed in 75% yield:[84]



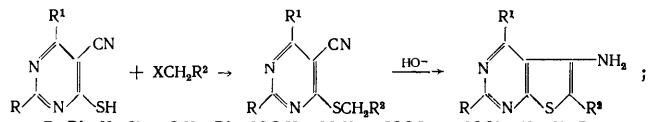
The reaction of ethyl glyoxalate with 6-aminouracils is of the type of aldol condensation and involves the formation of a bispyrimidine which cyclises under the influence of sodium bicarbonate to pyrrolo[2,3-*d*]pyrimidine:[85]





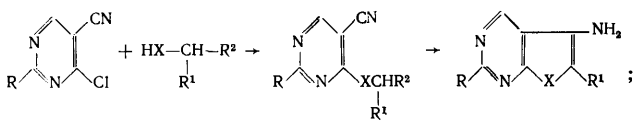
R=H, CH_3 .

Among the pyrimidines containing a substituent at the C(5) atom of the pyrimidine ring, the 5-cyano- and 5-ethoxycarbonyl derivatives are used in the syntheses of thieno- and pyrrolo-pyrimidines. Thus 5-cyano-6-mercaptopyrimidine can be alkylated by alkyl halides containing an active methylene group to form the 5-alkyl derivatives. The latter frequently cyclise in an alkaline medium to 5-aminothieno-[2,3-*d*]pyrimidines:[86,87]



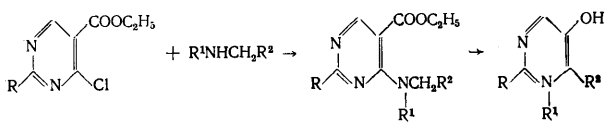
R, R^1=H, CH_3, C_6H_5; R^2=COC_6H_5, $COCH_3$, $COOC_2H_5$, COOH; X=Cl, Br .

When 6-chloro-5-cyanopyrimidines react with the corresponding mercapto- or amino-derivatives, intermediate 6-alkylthio- or 6-alkylamino-5-cyanopyrimidines are formed. These can be cyclised by a procedure analogous to that described above:[88,89]



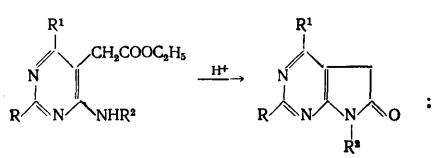
R=CH_3; R^1=$CH_2COOC_2H_5$; R^2=$COOC_2H_5$; X=S; R=C_6H_5; R^1=CN, $CONH_2$; R^2=H; X=NH, NCH_3 .

The reaction of 6-chloro-5-ethoxycarbonylpyrimidines with glycine derivatives leads to the formation of 5-hydroxypyrrolo[2,3-*d*]pyrimidines:[90-95]



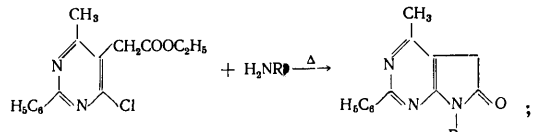
R=Alk, Ar; R^1=H, Alk; R^2=CN, $COOC_2H_5$.

Derivatives of pyrimidine-5-acetaldehydes and pyrimidine-5-acetic acids are widely used in the synthesis of pyrrolo-[2,3-*d*]pyrimidines. As stated previously,[1] the first synthesis of pyrrolo[2,3-*d*]pyrimidine was achieved on the basis of 4-aminopyrimidine-5-acetic acid. Several other early investigations in this field have been described:[96-99]



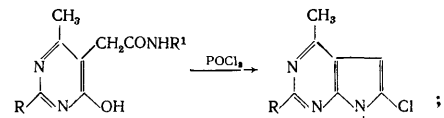
R=CH_3, C_6H_5, OH; R^1=H, OH; R^2=H, CH_3 .

When ethyl 6-chloropyrimidine-5-acetate is refluxed with amines, 6-oxopyrrolopyrimidines are also formed:[100,101]



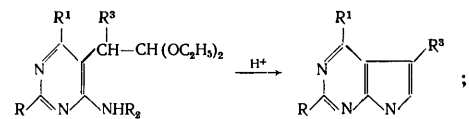
R=$CH_2CH_2OCH_3$, $CH_2C_6H_4Cl$-*p*, NH_2 .

6-Hydroxypyrimidine-5-acetamides cyclise on treatment with phosphoryl chloride to 6-chloropyrrolo[2,3-*d*]pyrimidines:[102-104]



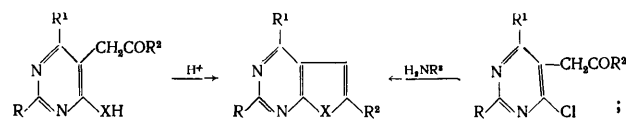
R=CH_3, $CH_2C_6H_4OCH_3$-*p*; R^1=Alk .

Many instances of the synthesis of pyrrolo[2,3-*d*]-pyrimidines from the acetals of 6-aminopyrimidine-5-acetaldehydes are described in the literature:[105-115]



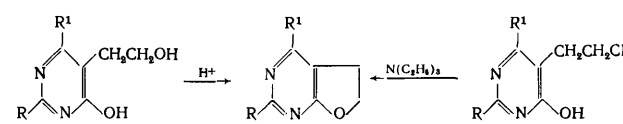
R=OH, SH, NH_2, H, Alk; R^1=H, OH, NH_2, Cl; R^2=H, Alk; R^3=H, CH_3 .

5-Acetonyl-6-hydroxypyrimidines and the corresponding 6-mercapto- and 6-amino-derivatives undergo an analogous reaction in an acid medium.[104,116-120] On the other hand, when 5-acetonyl-6-chloropyrimidines are heated with amines, pyrrolopyrimidines are formed:[118,121]



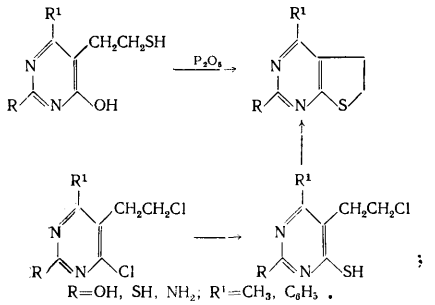
R=OH, SH, NH_2, $N(CH_3)_2$, H, CH_3, C_6H_5, $C_6H_5CH_2$; R^1=OH, Cl, CH_3, C_6H_5; R^2=CH_3, C_6H_5; R^3=Alk, Ar .

5-β-Hydroxy-, 5-β-halogeno-, and 5-β-mercapto-alkylamino-derivatives and 5-β-hydroxy-, 5-β-halogeno-, and 5-β-mercapto-ethyl derivatives of 6-hydroxy-, 6-amino-, or 6-chloro-pyrimidines have found applications in the syntheses of 5,6-dihydrofuro-, 5,6-dihydrothieno-, and 5,6-dihydropyrrolo-[2,3-*d*]pyrimidines. Thus, on treatment with thionyl chloride or sulphuric acid, 5-β-hydroxyethyl-6-hydroxypyrimidine cyclises to 5,6-dihydrofuropyrimidine.[122-127] The same compound can be obtained by treating 5-β-chloroethyl-6-hydroxypyrimidine with triethylamine:[128-130]



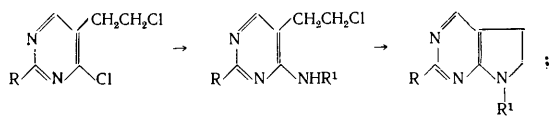
R=OH, SH, NH_2, $N(CH_3)_2$, SCH_3, H; R^1=OH, Cl, H, CH_3, C_6H_5 .

5,6-Dihydrothieno[2,3-*d*]pyrimidines have been obtained both from 6-hydroxy-5-β-mercaptoethylpyrimidine by treatment with phosphorus pentoxide and from 5-β-chloroethyl-6-chloropyrimidine by reaction with thiourea:[130-132]



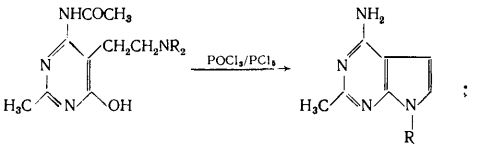
R=OH, SH, NH_2, R^1=CH_3, C_6H_5 .

5-β-Chloroethyl-6-chloropyrimidines can be made to react with amines to form the 6-amino-derivatives, which cyclise to 5,6-dihydropyrrolopyrimidines:[123,133–135]



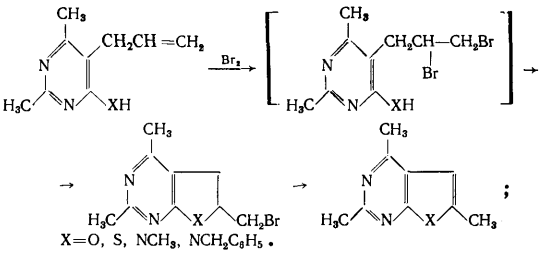
R=Cl, H, CH_3; R^1=Alk, Ar.

It is of interest to note that 7-alkylpyrrolo[2,3-*d*]-pyrimidine has been obtained by heating 5-β-dialkylamino-ethyl-6-hydroxypyrimidine with phosphoryl chloride and phosphorus pentachloride at 110 °C:[136]



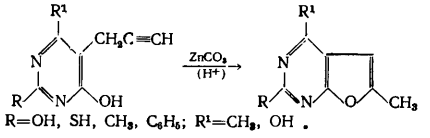
R=CH_3, C_2H_5 .

A convenient method of synthesis of furo-, thieno-, and pyrrolo-[2,3-*d*]pyrimidines from 5-allyl-6-hydroxy-, 5-allyl-6-mercapto-, and 5-allyl-6-amino-pyrimidines has been discovered recently.[137–139] When the above derivatives are brominated, 5-(2′,3′-dibromopropyl)pyrimidines are formed and then cyclise on refluxing in alcohol or DMF to the corresponding 6-bromomethyl-5,6-dihydro-derivatives. On treatment with sodium methoxide, these compounds give rise to 6-methylfuro-, 6-methylthieno-, and 6-methylpyrrolo-pyrimidines:



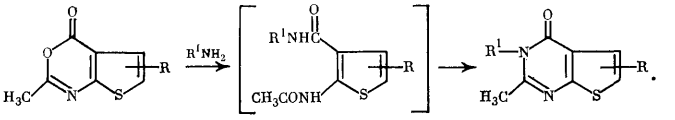
X=O, S, NCH_3, $NCH_2C_6H_5$.

It is known[140] that 6-hydroxy-2,4-dimethyl-5-propargyl-pyrimidine and 6-hydroxy-2-phenyl-5-propargylpyrimidine are converted into 6-methylfuro[2,3-*d*]-pyrimidines on treatment with zinc carbonate. An analogous reaction has been observed for 5-propargylbarbituric acid and the corresponding thiobarbituric acid in the presence of sulphuric acid:

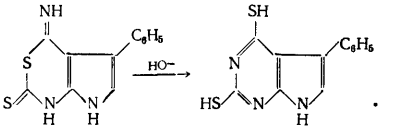


R=OH, SH, CH_3, C_6H_5; R^1=CH_3, OH .

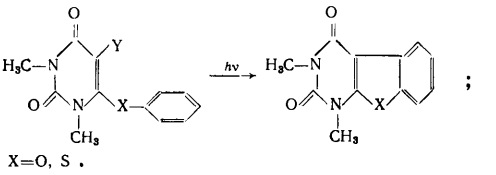
Only a few instances of the synthesis of thienopyrimidines from thieno[2,3-*d*]oxazines are described in the literature.[141–145] The intermediate 2-acylamino-3-carbamoylthiophens, which cyclise to thienopyrimidines on treatment with phosphoric acid, have sometimes been isolated in this process:



On treatment with alkali, 4-imino-5-phenyl-2-thiono-pyrrolo[2,3-*d*]thiazine rearranges to 2,4-dimercapto-6-phenylpyrrolo[2,3-*d*]pyrimidine:[146]

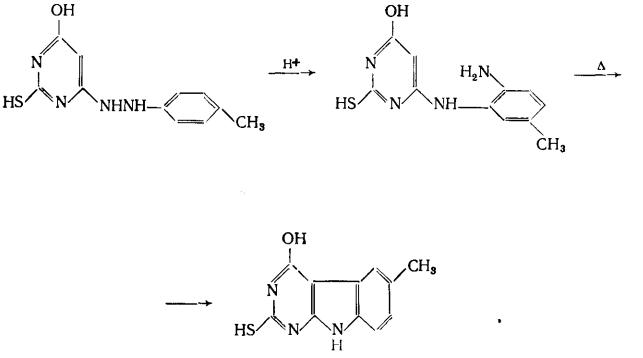


It has been observed[147] that the photolysis of 5-iodo-1,3-dimethyl-6-phenoxyuracil leads to the formation of a furo-pyrimidine in 1% yield, but the 6-phenylthio-analogue cyclises to the corresponding thienopyrimidine in 42% yield:

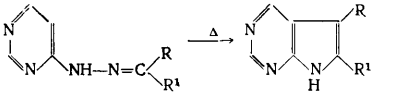


X=O, S .

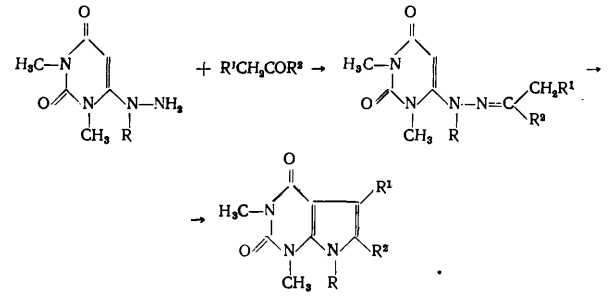
Mention should also be made of the method of synthesis of pyrrolopyrimidines from pyrimidinylhydrazines and hydrazones by analogy with the Fischer indole synthesis. Thus, on treatment with acids, 2-mercapto-6-*p*-tolylhydrazinouracil, gives rise to the stable 6-*o*-aminoanilino-2-mercaptouracil, which undergoes intramolecular cyclisation:[148]



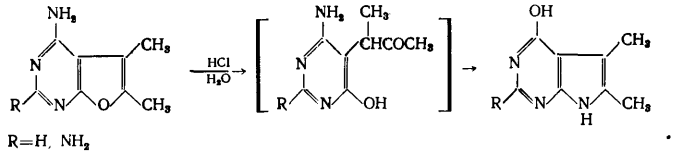
4-Pyrimidinylhydrazones undergo an analogous reaction on refluxing in ethylene glycol, but the yields are then low:[149]



The interaction of 6-hydrazino-1,3-dimethyluracil with ketones in ethylene glycol also affords pyrrolo[2,3-*d*]-pyrimidine:[150,151]



When an attempt was made to hydrolyse 4-aminofuro[2,3-*d*]-pyrimidine to the 4-hydroxy analogue with hydrochloric acid, 4-hydroxypyrrolo[2,3-*d*]pyrimidine was obtained.[152] Evidently the furan ring is opened during the reaction with the subsequent closure of the pyrrole ring. 2,4-Diamino-5,6-dimethylfuro[2,3-*d*]pyrimidine undergoes the same reaction:[79]

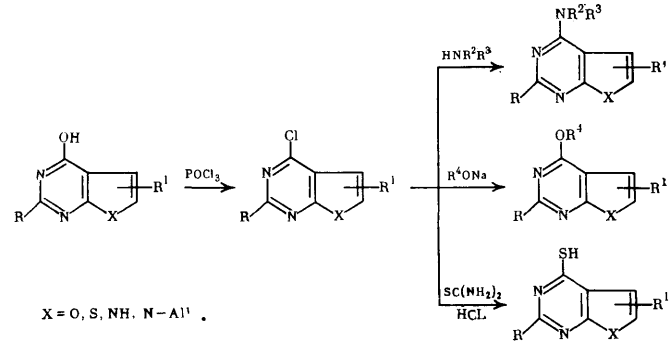


R=H, NH_2

III. CHEMICAL REACTIONS

Consideration of the electronic structures of furo-, thieno-, and pyrrolo-[2,3-*d*]pyrimidines shows that the pyrimidine ring in thse compounds is capable of nucleophilic substitution, while the C(5) and C(6) atoms of the five-membered rings are susceptible to attack by electrophiles.

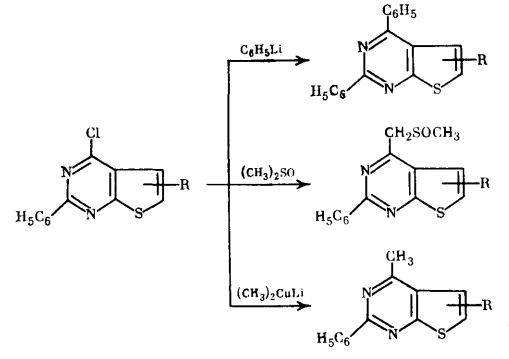
Thus the pyrimidine component of the molecule readily enters into reactions characteristic of pyrimidines. 4-Hydroxyfuro-, 4-hydroxythieno- or 4-hydroxypyrrolo-pyrimidines are readily converted into the 4-chloro-derivatives on treatment with phosphoryl chloride.[4,8,13,16,34,38,73,97,106-109,117-119,121,153-157] Next it is possible to obtain the 4-amino-, 4-hydrazino-, 4-alkoxy-, and 4-mercapto-derivatives of furo-, thieno-, and pyrrolo-[2,3-*d*]pyrimidines from these compounds by standard methods:[4,10,13,16,34,38,106,107,117-119,121,153-158,163,164]



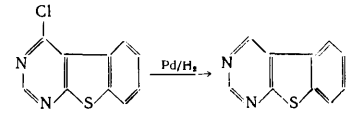
X = O, S, NH, N–Alk .

2,4-Dihydroxythieno[2,3-*d*]pyrimidines react with phosphoryl chloride to form 2,4-dichloro-derivatives, which are converted into a mixture of 4-amino-2-chloro- and 2-amino-4-chloro-thieno[2,3-*d*]pyrimidines on treatment with an alcoholic solution of ammonia at 100 °C.[156]

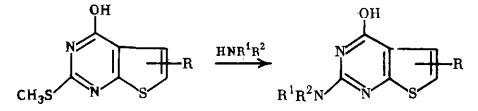
4-Chloro-2-phenylthieno[2,3-*d*]pyrimidine reacts with phenyl-lithium to form 2,4-diphenyl derivatives in 65% yield, the reaction with dimethyl sulphone affords the 4-methane-sulphinylmethyl derivative (80%), and the reaction with lithium dimethylcuprate gives rise to the 4-methyl derivative (82%):[16]



On treatment with [hydrogen and] a palladium catalyst, 4-chlorobenzothieno[2,3-*d*]pyrimidine loses a chlorine atom and is reduced to benzothieno[2,3-*d*]pyrimidine:[8]

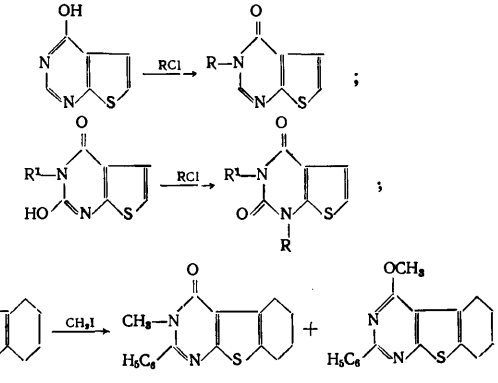


When 4-hydroxy-2-methylthiothieno[2,3-*d*]pyrimidine is acted upon by various amines, the corresponding 2-amino-derivatives are obtained:[165]



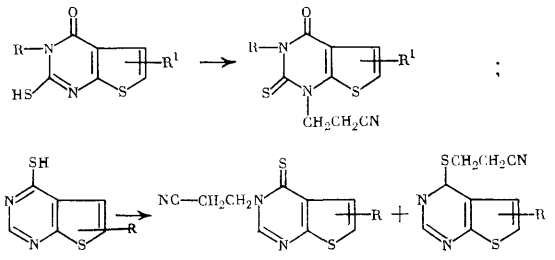
$-NR^1R^2 = N(CH_2)_5$, $N(CH_2CH_2)_2O$, $N(CH_2CH_2)_2NCH_3$, $NH(CH_2)_2OH$, $NHNH_2$.

A study of the alkylation of hydroxythieno[2,3-*d*]-pyrimidines yielded the following results: 4-hydroxythieno- and 2-hydroxo-4-oxothieno-pyrimidines react with alkyl halides to form *N*-derivatives, but 4-hydroxy-2-phenylthieno-pyrimidine reacts with methyl iodide in the presence of sodium hydride to form a mixture of the *N*(3)- and *O*-methyl derivatives in proportions of 1 : 1:[6,16]

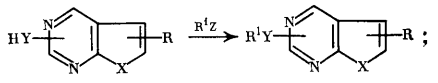


The cyanoethylation of 3-alkyl-2-mercapto-4-oxothieno-[2,3-*d*]pyrimidine proceeds via a nitrogen atom of the pyrimidine ring,[18] while 4-mercaptothienopyrimidine reacts

with acrylonitrile to form a mixture of *N*- and *S*-alkyl derivatives:[166]

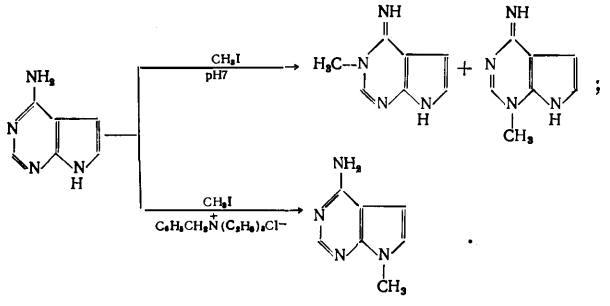


4-Mercaptothieno-, 2-mercaptothieno-, 2-selenothieno-, and 4-mercaptopyrrolo-[2,3-*d*]pyrimidines react with alkyl halides to form only the *S*(*Se*)-alkyl derivatives:[10,17,20,26,156,166–169]

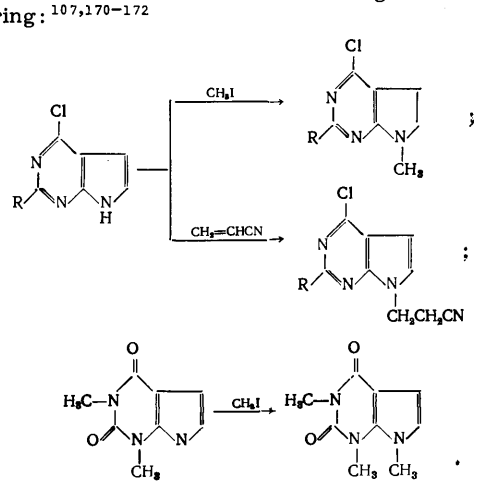


R^1 = Alk; X = S, NH; Y = S, Se; Z = Cl, Br, I.

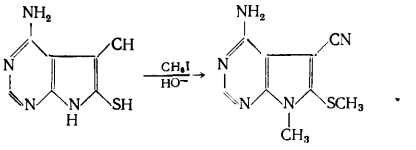
The study of the alkylation of 4-aminopyrrolo[2,3-*d*]-pyrimidine by methyl iodide yielded a 1 : 1 mixture of *N*(1)- and *N*(3)-methyl derivatives. However, the selective methylation of this compound involves the nitrogen atom of the pyrrole ring:[114]



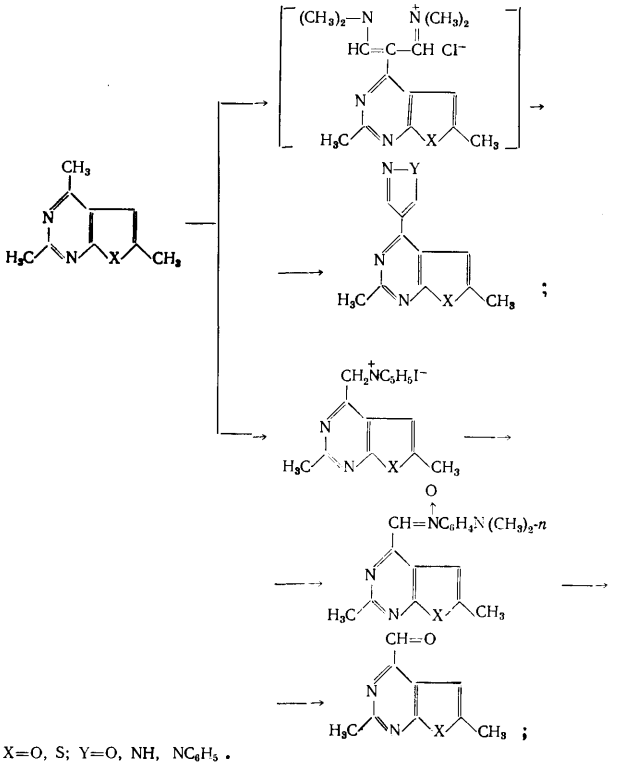
Like 2,4-dihydroxy-1,3-dimethylpyrrolo[2,3-*d*]pyrimidine, 4-chloropyrrolo[2,3-*d*]pyrimidine is methylated or cyanoethylated in an alkaline medium at the nitrogen atom of the pyrrole ring:[107,170–172]



The reaction of 4-amino-5-cyano-6-mercaptopyrrolo[2,3-*d*]-pyrimidine with methyl iodide results in the formation of 6-methylthio-7-methylpyrrolopyrimidine:[45]

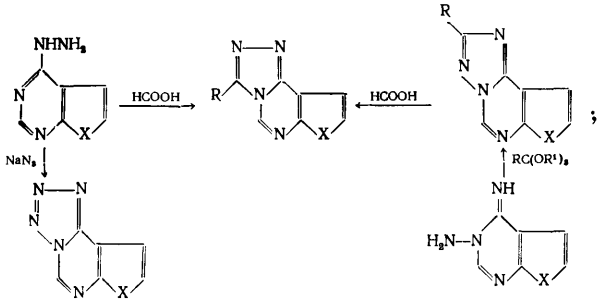


Certain reactions of the methyl group in 2,4,6-trimethyl-furo-, and 2,4,6-trimethylthieno-[2,3-*d*]pyrimidines have been investigated. Thus the corresponding pyrimidine-4-aldehydes have been obtained from these compounds by the Kröhnke method. It has been demonstrated by ^{1}H NMR that the most reactive methyl group at the C(4) atom of the pyrimidine ring is oxidised as a result of this reaction. The same methyl group reacts with Vilsmeier's reagent to form an unstable derivative of malonodialdehyde, which cyclises to 2,6-dimethyl-4-(4′-oxazolyl)- or 2,6-dimethyl-4-(4′-pyrazolyl)-furo(thieno)[2,3-*d*]pyrimidine on treatment with hydroxylamine or hydrazine:[173]



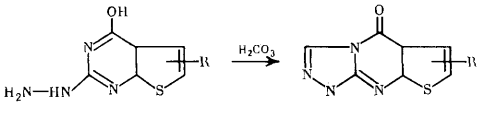
X=O, S; Y=O, NH, NC_6H_5.

Tricyclic systems can be obtained from certain furo- and thieno-pyrimidines by virtue of the presence of substituents in the pyrimidine ring. Thus, on treatment with formic acid or its ortho-ester, the 4-hydrazino-derivatives give rise to triazolothienopyrimidines,[10,38,52,156,174–176] while on treatment with sodium azide the products formed are tetrazolothieno-pyrimidines.[10,38,156,174,175] 3-Amino-4-iminofuropyrimidines and the corresponding thieno-derivatives cyclise on treatment with orthoformic or orthoacetic ester to the isomeric triazolo-derivatives, which undergo the rearrangement shown in the scheme below when acted upon by formic acid:[52,176]

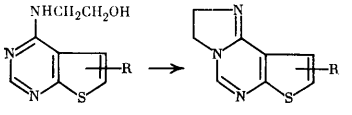


X=O, S; R=H, CH_3; R^1=CH_3, C_6H_5 .

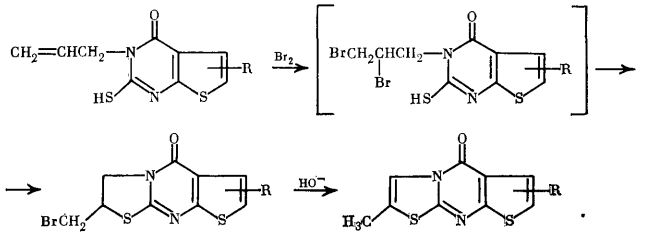
When acted upon by carbonic acid, 2-hydrazino-4-hydroxythieno[2,3-*d*]pyrimidine also cyclises to the corresponding triazolothienopyrimidine:[165]



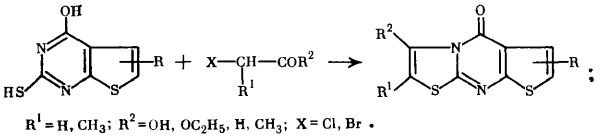
Imidazolinothienopyrimidine has been obtained from 4-β-hydroxyethylaminothieno[2,3-*d*]pyrimidine:[38,175]



3-Allyl-2-mercapto-4-oxothieno[2,3-*d*]pyrimidines are convenient starting materials in the synthesis of thiazolothienopyrimidines. On treatment with bromine, these compounds give rise to the corresponding tricyclic systems:[18,23-25,177,178]

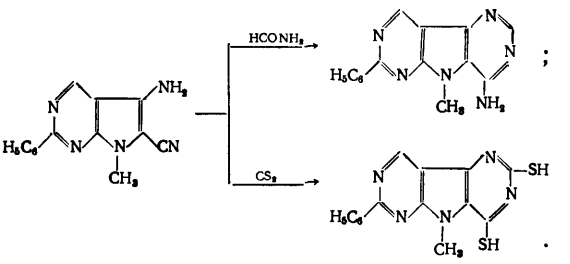


The same system can be obtained by the reaction of α-halogenocarbonyl compounds with 4-hydroxy-2-mercaptothieno[2,3-*d*]pyrimidines:[179]

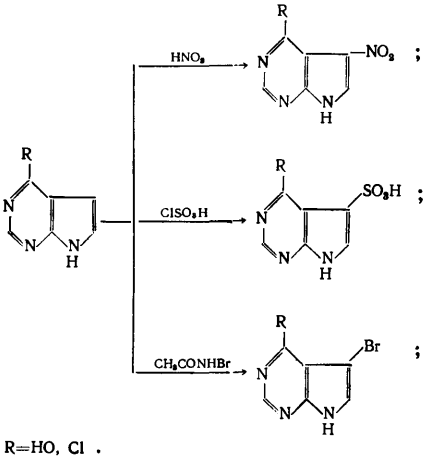


R^1=H, CH_3; R^2=OH, OC_2H_5, H, CH_3; X=Cl, Br .

Tricyclic heteroatomic systems have also been synthesised with participation of substituents in the five-membered ring. Thus 5-amino-6-cyano-2-phenylpyrrolo[2,3-*d*]pyrimidine reacts with formamide to form the corresponding aminopyrrolo[2,3-*d*;4,5-*d'*]dipyrimidine, while the reaction with carbon disulphide yields the dimercapto-derivative:[89]

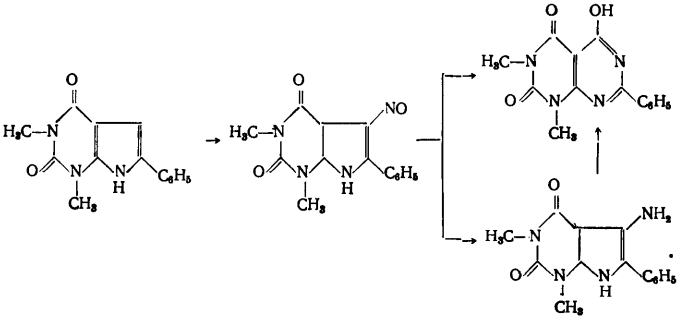


In considering reactions involving electrophilic substitution in the pyrrole ring, mention should be made of a study[157] in which 4-hydroxy- and 4-chloro-pyrrolo[2,3-*d*]pyrimidines were nitrated, chlorosulphonated, and brominated. In all cases the reaction involves the β-position in the pyrrole ring:



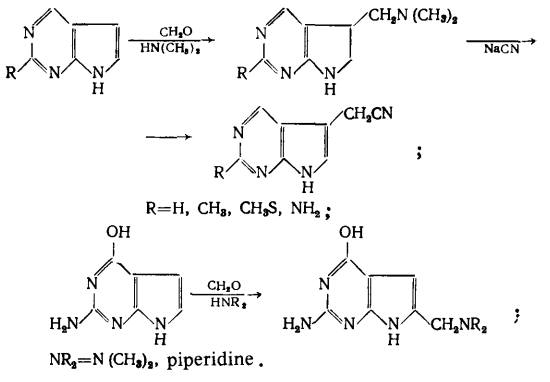
R=HO, Cl .

The nitrosation of 1,3-dimethyl-6-phenylpyrrolo[2,3-*d*]-pyrimidine also takes place in the β-position of the pyrrole ring.[78] Subsequently the 5-nitroso-derivative can undergo the Beckmann rearrangement with formation of a pyrimidopyrimidine. The reduction of the nitroso-group results in the formation of 5-aminopyrrolopyrimidine which also rearranges to a pyrimidopyrimidine on treatment with lead acetate:[180]

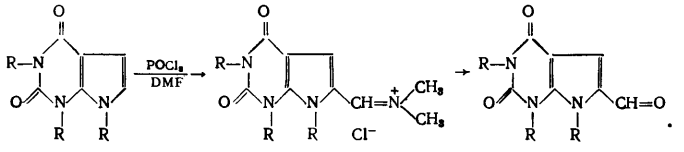


Pyrrolopyrimidines undergo the Mannich reaction, but the available literature data are somewhat contradictory. 2-Substituted pyrrolo[2,3-*d*]pyrimidines react with formaldehyde and dimethylamine in the presence of sodium acetate to form the 5-dimethylaminomethylene derivatives,[181] which can be converted into 5-cyanomethylenepyrrolopyrimidines. However, it has been reported[113] that 2-amino-4-hydroxypyrrolo-[2,3-*d*]pyrimidine reacts with formaldehyde and dialkylamines

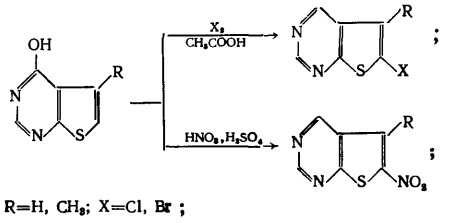
in the presence of acetic acid to form the 6-dialkylaminomethylene derivative:

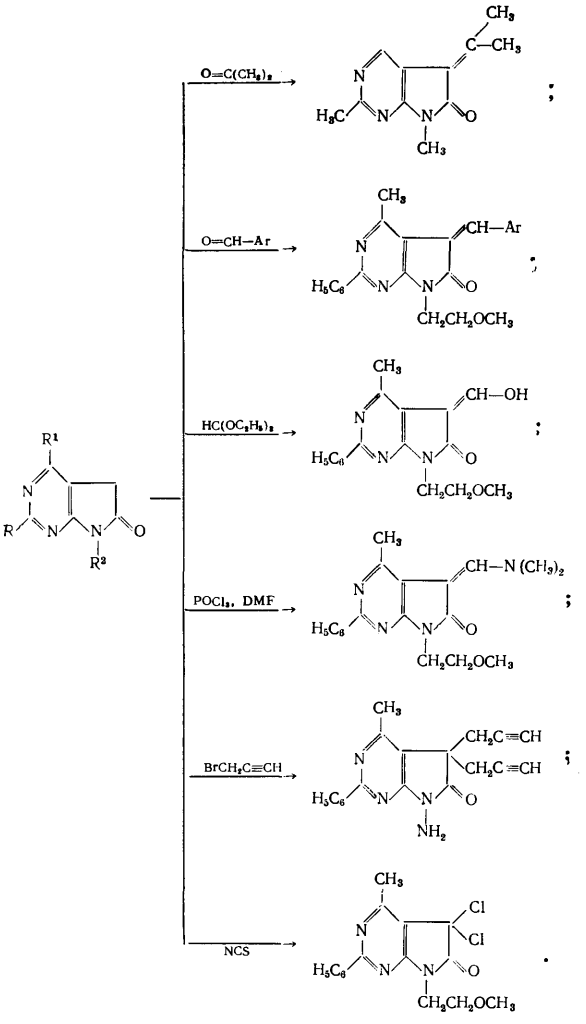


1,3,7-Trialkyl-2,4-dioxopyrrolo[2,3-*d*]pyrimidine reacts with Vilsmeier's reagent also in the α-position in the pyrrole ring to form the corresponding aldehyde:[182]



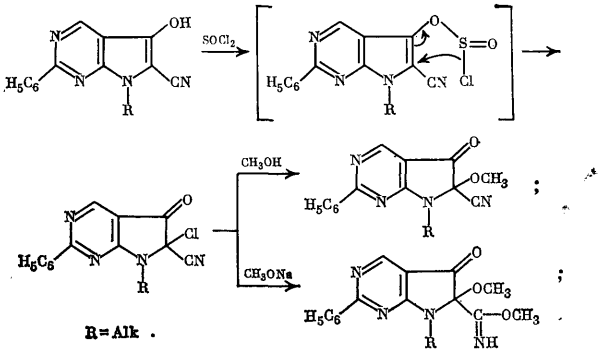
Certain electrophilic substitution reactions of 4-hydroxythieno[2,3-*d*]pyrimidines which involve the α-position in the thiophen ring, have been investigated:[6,61,174]



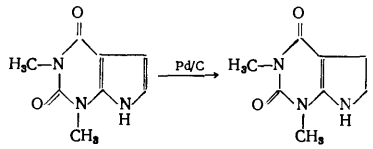


It has been observed that the methylene group in the pyrrole ring of 6-oxopyrrolopyrimidines is very reactive and reacts with aldehydes,[101] ketones,[98] propargyl bromide,[100] orthoformic ester, Vilsmeier's reagent, and *N*-chlorosuccinimide[101] to form the corresponding 5-substituted 6-oxopyrrolo[2,3-*d*]pyrimidines.

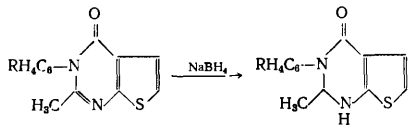
Kim and Santilli[183,184] investigated the reaction of thionyl chloride with 7-alkyl-6-cyano-5-oxo-2-phenylpyrrolo[2,3-*d*]-pyrimidines and established that it involves the oxicative chlorination at the α-position in the pyrrole ring:



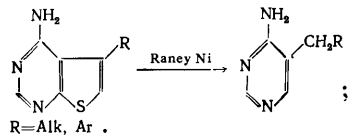
Several instances of the reduction of thieno- and pyrrolopyrimidines in the presence of various catalysts have been described in the literature. When 1,3-dimethyl-2,4-dioxopyrrolo[2,3-*d*]pyrimidine is treated with a palladium catalyst, the corresponding 5,6-dihydro-derivative is formed in 66% yield:[185]



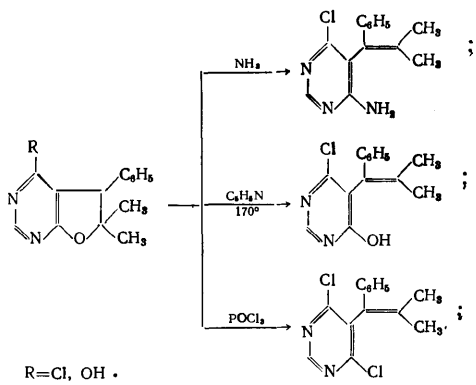
Sodium tetrahydroborate reduces 2-methyl-4-oxo-3-phenylthieno[2,3-*d*]pyrimidine to the 1,2-dihydro-derivative:[186]



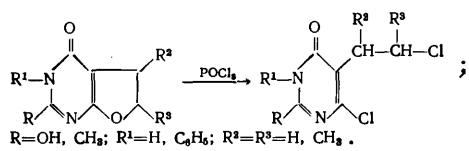
4-Aminothieno[2,3-*d*]pyrimidine containing a substituent in the 5-position in the thiophen ring gives rise to a 4-amino-5-substituted pyrimidine on treatment with Raney nickel:[47-49]



Among other reactions involving the opening of the five-membered ring, mention may be made of the formation of 5-vinylpyrimidines from the corresponding 5,6-dihydro-6,6-dimethyl-5-phenylfuropyrimidines on treatment with ammonia or phosphoryl chloride:[34,187]

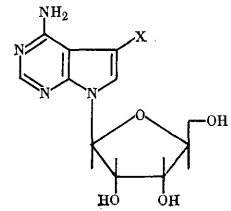


When acted upon by phosphoryl chloride, certain 5,6-dihydrofuropyrimidines give rise to 6-chlor-5-β-chloroethylpyrimidines:[130,188]



IV. BIOLOGICAL PROPERTIES

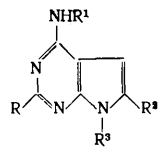
It was discovered in the 1960's that the antibiotics tubercidin, toyocamycin, and sangivamycin are derivatives of pyrrolo[2,3-*d*]pyrimidine:[51,189-191]



X = H (tubercidin)
X = CN (toyocamycin)
X = $CONH_2$ (sangivamycin)

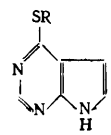
Toyocamycin actively inhibits the growth of various microorganisms,[192-194] tubercidin exhibits an analogous activity,[195,196] while sangivamycin shows a distinct antitumour activity, becoming involved in DNA and RNA synthesis.[191,197] There exists a good review on these antibiotics.[198]

4-Aminopyrrolo[2,3-*d*]pyrimidine is also an inhibitor of the growth of various micro-organisms[73] and its derivatives possess bactericidal,[111] hypotensive, anticonvulsant, and tranquilising properties[107,160] and exhibit an antimitotic activity.[121]



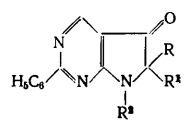
R=H, CH_3, OH, H, NH_2; R^1, R^3=H, Alk, Ar; R^2=H, CH_3

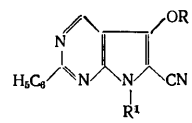
4-Mercaptopyrrolo[2,3-*d*]pyrimidine is the 5-deaza-analogue of the familiar antitumour preparation 6-mercaptopurine, but it does not exhibit a pronounced anticancer activity. Nevertheless 4-alkylmercaptopyrrolopyrimidines do possess antineoplastic properties.[167-169]



R=H, Alk, $(CH_2)_n CONHR^1$;
R^1 = aminoacid residue

Among 5-hydroxy-2-phenylpyrrolo[2,3-*d*]pyrimidines, compounds have been discovered which act on the central nervous system as depressants.[92-95,184]

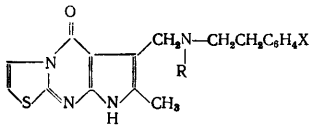


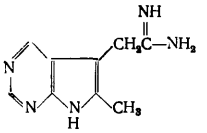


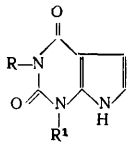
R=Cl, OCH_3, OC_6H_5, OC_3H_7-iso; R=H, CH_3, $SO_2C_6H_5$; R^1=CH_3, R^1=CN, $C(OCH_3)$=NH; R^2=Alk C_2H_5, C_4H_9

5-Alkylaminomethyl derivatives of thiazolopyrrolopyrimidines prevent the formation of blood clots,[199] while 5-amidinomethyl-6-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidine has a powerful ganglion stimulating activity.[200]

It has also been reported that 1,3-dialkyl-2,4-dioxopyrrolo[2,3-*d*]pyrimidines exhibit sedative and antipyretic activities.[151]

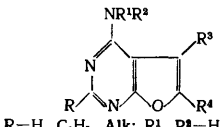




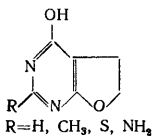


R, R¹=Alk

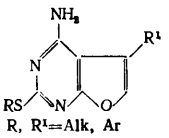
There are also biologically active compounds among furo-[2,3-*d*]pyrimidines. Thus 4-aminofuro[2,3-*d*]pyrimidines are muscle relaxants[119] and exhibit sedative, antihistamine, and diuretic properties.[53,54] 2-Substituted 4-hydroxy-5,6-dihydrofuropyrimidine reduces the cholesterol content in the blood,[127] while 2-alkylthio-4-aminofuro[2,3-*d*]pyrimidine shows an antiulcer activity:[81]



R=H, C_6H_5, Alk; R^1, R^2=H, Alk, Ar; R^3, R^4=Alk, Ar, NO_2.

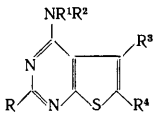


R=H, CH_3, S, NH_2



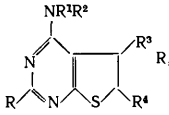
R, R^1=Alk, Ar

Numerous compounds with a wide variety of different types of physiological activity have been discovered among synthetic thienopyrimidines. Derivatives of 4-aminothieno[2,3-*d*]pyrimidines exhibit bactericidal, trichomonacidal,[13] antiradiation, antimalarial,[43] antihistamine,[153] acaricidal, insecticidal, and fungicidal properties[161,162] and prevent the formation of clots.[29]



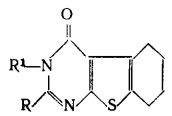
R=Ar, NH—Alk; R^1, R^2=H, CH_3, $(CH_2)_2$, NH—Alk, $SO_2C_6H_5$, OC_6H_5, Ar, Alk; R^3, R^4=H, CH_3, $(CH_2)_4$

4-Amino-5,6-dihydrothieno[2,3-*d*]pyrimidines possess sedative, diuretic, and antihistamine activities and function as muscle relaxants.[56,163,164]

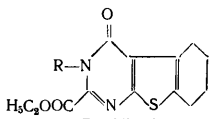


R, R^1, R^2, R^3, R^4=H, Alk, Ar

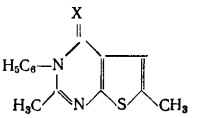
Depressants of the central nervous system, diuretics, and hypotensive, antipyretic,[144,145] analgesic, sedative,[30] antiallergic,[37,39] and hypnotic[201] substances have been discovered among 4-oxothienopyrimidines.



R=CH_3, C_2H_5; R^1=H, CH_3, C_6H_5.

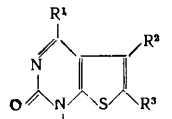


R=Alk, Ar

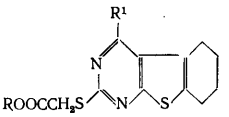


X=O, NC_6H_5

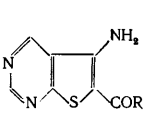
4-Aryl-2-oxothienopyrimidines also exhibit analgesic and diuretic activites;[58,66] 2-alkylthio-4-aryl derivatives show anticlotting, antipyretic, and analgesic activities and reduce the sugar content in the blood.[63] 5-Amino-6-carboxythieno-[2,3-*d*]pyrimidine exhibits bactericidal, analgesic, and diuretic activities and has an antipyretic effect.[86]



R=H, Alk; R^1=Ar; R^2=H, CH_3; R^3=H, CH_3, Cl, NO_2.



R=H, CH_3, C_2H_5; R^1=Ar



R=Ar, NR_2

Thus the foregoing findings permit the conclusion that derivatives of furo-, thieno-, and pyrrolo-[2,3-*d*]pyrimidines are of considerable interest as physiologically active substances, which has attracted the attention of numerous investigators to these compounds.

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Metal Carbonyl Complexes with Ligands of Biological Origin

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The methods of synthesis, structure, and physicochemical and chemical properties of transition metal carbonyl derivatives containing biological ligands, namely porphyrins, nucleic bases and nucleosides, aminoacids, and peptides, are examined. The possibility of using metal carbonyl complexes with biological ligands in various branches of chemistry is discussed. The bibliography includes 124 references

CONTENTS

I. Introduction 277
II. Porphyrin derivatives of metal carbonyl compounds 278
III. Complexes of metal carbonyls with nucleic bases and nucleosides 282
IV. Metal carbonyl complexes with aminoacid and peptide ligands 284

INTRODUCTION

The rapid growth of interest in recent years in the chemistry of transition metal complexes with ligands of biological origin is due to the extremely important role which metal ions play in a wide variety of biological processes.[1-6] The multifunctionality of metal ions in biological systems is undoubtedly associated with the wide variety of the chemical and stereochemical characteristics of the complexes formed by metals with protein molecules. The problem of the elucidation of the nature of the metal–protein interaction has therefore assumed special importance. Model compounds which are usually inorganic coordination compounds containing ligands of the acido-type in addition to biological ligands, namely porphyrins, amides, aminoacids, low-molecular-weight peptides, etc., are usually employed for the solution of this complicated problem. However, these complexes do not as a rule contain atoms or groups changes in the characteristics of which would permit fairly reliable inferences to be drawn about the steric and electronic features of the molecules investigated. Furthermore, the interaction of metal ions with biomolecules in an aqueous medium, usually employed for the synthesis in an investigation of inorganic complexes, is hardly an adequate model for the real interactions within the bulky protein molecules, which possess appreciably hydrophobic properties.

Numerous organometallic complexes of transition metals of various bioligands have been obtained in recent years. One can apparently speak of the establishment at the present time of a new branch of science—*bioorganometallic chemistry*, which is concerned with the study of transition metal complexes which contain, apart from the bioligands, at least one organic group linked to the metal atom via a metal carbon bond. Vitamin B_{12} is a representative of this class of compounds discovered in nature.

In contrast to inorganic coordination compounds, organometallic complexes are as a rule volatile and soluble in organic solvents. This makes possible a wide-scale use of methods such as mass spectrometry, NMR involving different nuclei, various types of vibrational spectroscopy, etc., for their investigation. Metal carbonyl complexes constitute a large class of such compounds. The presence in these substances of carbonyl groups linked to the metal atom, which are very sensitive to changes in the electronic and stereochemical characteristics of the metal atom and its ligand environment, and have highly characteristic infrared and Raman spectroscopic properties, makes it possible to establish in many instances the character of the metal–ligand bonds and the disposition of the ligands around the central metal atom.

Thus organometallic compounds of transition metals with ligands of biological origin have many important advantages over traditional inorganic compounds. It therefore appears likely to be useful to employ them as model systems for the investigation of the interaction between metal atoms and the active centres of protein molecules. It is noteworthy that the reactions with carbon monoxide, leading to the formation of metal carbonyl complexes, have already found extensive applications in the study of the properties of natural metal–porphyrin systems and their synthetic models.

The study of organometallic complexes with bioligands proved useful for the modelling of various catalytic processes *in vivo* with participation of metalloenzymes, for example, the fixation of nitrogen, the oxidation of alkanes, etc. Derivatives of metal carbonyls can also be used to introduce transition metals into protein molecules as labels, to impart new transport properties to biomolecules, and, in particular, to increase their solubility in organic solvents and fats, and as intermediates in the synthesis of proteins and other biologically active compounds. Furthermore, it appears useful to use metal carbonyl derivatives for the synthesis and study of biologically active complexes of those transition metals whose content in the biosphere increases as a result of anthropogenic factors.

This review deals with the results of studies in recent years on the synthesis and chemical and physicochemical properties of derivatives of metal carbonyls with certain most important biological nitrogen-containing ligands: porphyrins, nucleic bases and nucleosides, aminoacids, and peptides. So far as the present author is aware, no reviews devoted to this branch of chemistry have been published hitherto with the exception of the paper by Tsutsui,[7] which considers mainly the results of the author's studies of metal carbonyl porphyrin complexes. The present author thought it desirable to include in this review certain data on non-carbonyl organometallic aminoacid and peptide complexes of

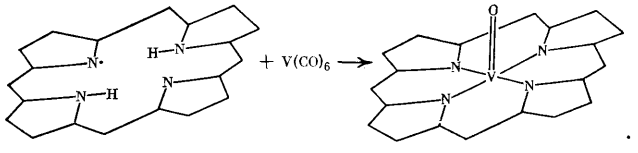
transition metals whose methods of synthesis and properties are close to those for the analogous metal carbonyl compounds.

II. PORPHYRIN DERIVATIVES OF METAL CARBONYL COMPOUNDS

Two discoveries at the beginning of the 1950's served as a direct stimulus for the investigation of metal carbonyl porphyrin complexes. The organometallic nature of one of the most important natural biologic reactive compounds, the vitamin B_{12} coenzyme, was established. In this compound the cobalt atom, coordinated to a corrin macroring which largely resembles the porphyrin macroring, is linked via a σ-bond to an alkyl carbon atom.[8,9] In addition, it has been elucidated that the cause of the deactivation of haemoglobin by carbon monoxide is the formation of a stable iron-porphyrin carbonyl complex the stretching vibration frequency of the C≡O bond of which in the infrared spectrum [ν(CO) = 1970 cm^{-1}] is close to the analogous frequencies of other derivatives of iron carbonyl.[10]

The study of the reactions of metal carbonyls with various porphyrins, initiated in the middle of the 1960's,[11,12] not only made it possible to synthesise a number of new metalloporphyrin complexes but also led to the establishment of certain hitherto unknown characteristics of the behaviour of porphyrin macrorings.

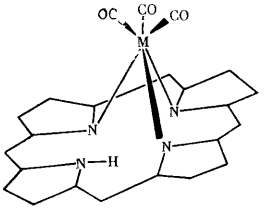
When vanadium hexacarbonyl reacts with H_2MP† in an inert atmosphere in decane at 170 °C, all the carbonyl groups are split off, the metal atom is oxidised, and the vanadyl complex (MP)V = O is formed:[13,14]



An analogous complex has been obtained[15] by the interaction of H_2AEP with (η^5-C_5H_5)V(CO)$_4$. The nature of the oxidant both in the reactions quoted above and in other processes involving a change in the oxidation state of the metal atom has not been elucidated. The most probable source of oxygen is apparently CO, which can disproportionate at high temperatures in the presence of transition metals.

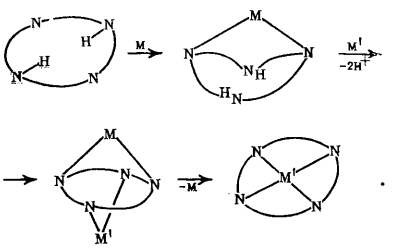
Heating of chromium hexacarbonyl and H_2MP in decane at 170 °C leads to the formation of chromium(II) porphyrinate (MP)Cr and complexes of the same composition have been obtained by heating H_2PP with nickel and cobalt carbonyls.[12,14] However, when H_2TPP interacts with Mo(CO)$_6$ in decalin, more extensive oxidation of the metal atom takes place and the oxomolybdenum complex (TPP)MoO(OH) is formed.[16]

A series of unusual complexes have been obtained in the reactions of porphyrins with Group VII metal carbonyls. Depending on the reactant ratio, mono- or bi-metallic complexes are formed on heating H_2MP or H_2TPP and $M_2(CO)_{10}$ (M = Tc or Re) in decane or decalin.[17-22] In the presence of a deficiency of the carbonyl, the monometallic compounds (HL)M(CO)$_3$(I), where L = MP and M = Tc or Re or L = TPP and M = Re, have been obtained. The infrared spectra of the complexes (I) contain two (three for Tc derivatives) ν(CO) bands at 2010–2025 and 1875–1900 cm^{-1}, which are characteristic of complexes of the type XM(CO)$_3$L$'_2$ (X = Hal, Alk, or Ar and L$'$ = Py or amine) and a ν(NH) band at 3350–3380 cm^{-1}. At room temperature the ^{1}H NMR spectra show the signal of one proton linked to the pyrrole nitrogen atom in the range δ = −4.0–−5.0 p.p.m., as well as the signals of the non-equivalent methylidyne and β-pyrrole hydrogen atoms. With increase of temperature, the signals of the methylidyne and β-pyrrole hydrogen atoms merge in the ^{1}H NMR spectra, indicating a dynamic behaviour of the metal tricarbonyl groups in relation to the porphyrin macroring. The free energy of activation for this process, involving the complex (HMP)Tc(CO)$_3$, is $\Delta G^{\neq}$ = 19.3 ± 2 kcal mol^{-1}.[23] On the basis of spectroscopic data, it has been suggested that the metal atom in complex (I) is not located in the plane of the porphyrin ring and is linked to only three pyrrole nitrogen atoms.



(I) M = Tc, Re

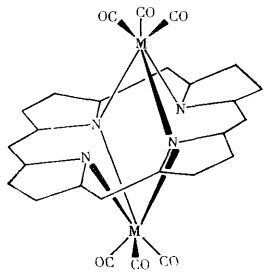
The effect of copper(II) acetate on (HMP)Re(CO)$_3$ at room temperature leads to the substitution of the rhenium tricarbonyl group and the formation of copper porphyrinate.[22] It has been reported[24] that unstable bimetallic complexes are formed in the analogous reactions with Ag^+, Hg^{2+}, and Pb^{2+} salts. These data agree well with the mechanism proposed previously[25] for the insertion of metal ions in porphyrin rings. It has been suggested that one of the metal atoms is initially coordinated to several nitrogen atoms of the macroring, which results in a breakdown of the coplanarity of the latter, after which the attack by the second metal atom from the opposite side of the macroring leads to the formation of an unstable bimetallic complex, which is rapidly converted into a stable metalloporphyrin:



†The following notation has been adopted for porphyrins in the present study: H_2MP = dimethyl ether of *meso*-porphyrin IX, H_2AEP = aetioporphyrin, H_2TPP = tetraphenyl-*meso*-porphin, H_2PrTPP = tetrakis(*p*-isopropylphenyl)-*meso*-porphin, H_2PP = dimethyl ether of protoporphyrin IX, H_2HeP = dimethyl ether of haematoporphyrin X, H_2OEP = octaethylporphyrin, MeHOEP = *N*-methyloctaethyl-porphyrin, and EtHOEP = *N*-ethyloctaethylporphyrin. To simplify the representation, the double bonds and substituents in the porphyrin macrorings have been omitted in the reaction schemes and structural formulae.

Treatment of porphyrins with an excess of Group VII metal carbonyls results in the formation of the bimetallic complexes $L[M(CO_3)]_2$ (II), where L = MP or TPP and M = Tc or Re, whose infrared spectra are analogous to those of compounds (I) in the ν(CO) region.[17-24] The reaction proceeds via the intermediate formation of monometallic complexes (I), which are capable of combining with yet another metal tricarbonyl group. Thus treatment of the monorhenium complex $(HMP)Re(CO)_3$ with technetium carbonyl yielded the mixed bimetallic complex $(MP)[Tc(CO)_3][Re.(CO)_3]$.[21,22,26] The bimetallic compounds (II) are probably thermodynamically more stable than (I). It has been found[21] that $(HMP)Tc(CO)_3$ disproportionates irreversibly in boiling decalin with formation of $(MP)[Tc(CO)_3]_2$ and the free porphyrin.

The structure of two bimetallic compounds $(TPP)[M(CO)_3]_2$ (M = Tc or Re) has been established by X-ray diffraction.[21,26,27]



(II) M = Tc, Re

The metal tricarbonyl groups are located on both sides of the planar porphyrin macroring and each metal atom, separated from the plane of the porphyrin by ~1.40 Å, is linked to only three nitrogen atoms. Thus in these compounds the porphyrin behaves as a hexadentate ligand. The metal–nitrogen distances are non-equivalent: one of them (2.15 Å for M = Re and 2.142 Å for M = Tc) corresponds to the M–N σ-bond and the other two, whose lengths are ~2.40 Å, are apparently the M ← N donor–acceptor bonds. The distances between the metal atoms (3.127 Å for M = Re and 3.101 Å for M = Tc) are close to the metal–metal bond lengths in the dinuclear decacarbonyls $M_2(CO)_{10}$, but calculation of the number of electrons shows that there should be no direct metal–metal covalent bonding in complexes (II).

The oxidation-reduction properties of the tetraphenylporphyrin complexes (I) and (II) for M = Re have been investigated by polarographic methods.[28-31] In solutions in CH_2Cl_2 or dimethylformamide the complexes undergo two-electron oxidation and reduction in stages at a platinum electrode with formation of chemically stable products in each stage. The polarographic waves for the complexes are analogous to the waves for reversible oxidation-reduction processes involving the free porphyrin:

$$H_2L^{2+} \xleftarrow{-e^-} H_2L^{+} \xleftarrow{-e^-} H_2L \xrightarrow{+e^-} H_2L \xrightarrow{+e^-} H_2L^{2-}.$$

However, the potentials are displaced towards more positive values for the cathodic processes and more negative values for the anodic processes. The ease of reduction decreases in the sequence

$$(TPP)[Re(CO)_3]_2 > (HTPP)Re(CO)_3 > H_2TPP,$$

which indicates the involvement of the rhenium tricarbonyl groups in the delocalisation of the charge of the porphyrin ring. The electrochemical oxidation of complex (I) is irreversible and leads to the formation of a bimetallic product, probably with a structure similar to that of compounds (II).

The reaction of $(TPP)[Re(CO)_3]_2$ with $SbCl_5$ at −70 °C in CH_2Cl_2 led to the isolation of three thermally unstable ionic complexes which are sensitive to moisture: $\{(TPP)[Re.(CO)_3][Re(CO)_3Cl]\}^+[SbCl_6]^-$ (III), $\{(TPP)[Re(CO)_3.Cl]_2\}^{2+}2[SbCl_6]^-$ (IV), and $\{(TPP)[Re(CO)_3]_2\}^+[SbCl_6]^-$ (V). In inert solvents all these compounds decompose with regeneration of the initial compound (II). It has been suggested that compounds (III) and (IV) possess Re–Cl bonds. The structure of the cation in the complex (V), elucidated as a result of X-ray diffraction analysis, proved to be very similar to that of the uncharged complex (II), but the distance between the rhenium atoms, which is 2.95 Å, enabled the authors[32] to conclude that an Re–Re bond passing through the aperture in the porphyrin macroring, is present in this compound. Such structures of the pseudorotaxane type had not been known previously.

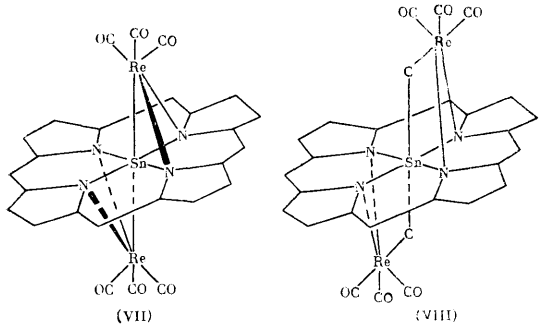
Prolonged heating of complexes (II, L = MP, M = Tc or Re) leads to the formation of insoluble products containing metal carbonyl groups with ν(CO) = 2044 and 1925 cm^{-1}. The structure of these compounds is unknown, but it has been suggested that they are polymers formed as a result of the coordination of the metal atoms to the ester groups linked to the porphyrin ring.[18]

On refluxing H_2OEP with $ClRe(CO)_5$, $BrRe(CO)_5$, or $[BrRe(CO)_4]_2$ in decalin, dark red crystalline ionic compounds $[H_3OEP]^+[Re_2(CO)_6X_3]^-$ (VI) (X = Cl or Br) were obtained together with the bimetallic complex of type (II). Solutions of these complexes in CH_2Cl_2, tetrahydrofuran, or methyl acetate are stable, but in alcohols, acetone, or in water they rapidly decompose with liberation of the free porphyrin. Prolonged heating of compound (VI) in aprotic solvents leads to the formation of the monorhenium complex (I). It has been established by X-ray diffraction of compound (VI, X = Cl) that the latter has no direct bond between the porphyrin macroring and the rhenium atoms. It is noteworthy that, on heating $ClRe(CO)_5$ and H_2TPP in decalin, complexes of type (VI) are not formed and only $[H_4TPP]^{2+}.2Cl^-$ has been isolated as a result of the reaction.[33,34]

Several unusual compounds have been obtained as a result of the reactions of $Re_2(CO)_{10}$ with tetraphenylporphyrin derivatives of non-transition metals. On heating $Re_2(CO)_{10}$ and $(TPP)SnCl_2$ in decalin at 180 °C, a dark-green crystalline complex $(TPP)Sn[Re(CO)_3]_2$ (VII) is formed and a symmetrical structure with an Re–Sn–Re bond chain has been proposed for it.[35] Compounds of analogous composition have also been obtained on interaction of rhenium carbonyl with zinc, magnesium, and calcium porphyrinates, although it is unlikely that the ions of these metals can form σ-bonds with the rhenium atoms.

A comparatively slight decrease of the temperature of the reaction between $Re_2(CO)_{10}$ and $(TPP)SnCl_2$ (decalin, 160–165 °C) led to the formation of another, red complex $(TPP).Sn[CRe(CO)_3]_2$ (VIII) whose structure has been established by X-ray diffraction.[36] Two carbide C atoms, each of which is linked to the tin atom located at the centre of the porphyrin macroring and to the $Re(CO)_3$ group, were found in this compound. The Sn–C bond length is close to that of a

single bond, while the short C–Re distances (1.75 Å) led to the conclusion[36] that the bond between these atoms has the character of a triple bond.

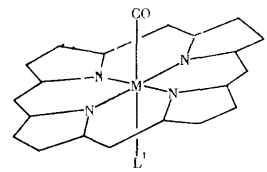


(VII) (VIII)

The C–Sn–C linear fragment is perpendicular to the plane passing through the four nitrogen atoms and the tin atom; the Sn–C–Re angle is 138.5°. Formally the rhenium atoms in complexes (VII) and (VIII) are electronically and coordination unsaturated since only three CO groups are linked to each of them, apart from the Sn or C atoms. However, the infrared spectra of these complexes show identical ν(CO) frequencies of 2000, 1995 and 1920 cm^{-1}, which are close to the analogous frequencies in the spectra of compounds of the type $XRe(CO)_3L_2$, where L is a neutral nitrogen-containing ligand. It is therefore logical to suppose that the Re atoms in the complexes (VII) and (VIII) undergo electronic and coordination saturation as a result of interaction with the pyrrole nitrogen atoms and (or) the π-electron system of the porphyrin ring, despite the fact that the rhenium atoms in complex (VIII) are separated from the plane of the ring by more than 3.5 Å.

The reactions of the iron carbonyls $Fe(CO)_5$ and $Fe_3(CO)_{12}$ with H_2MP and H_2PP proceed with elimination of all the CO groups and the formation of non-carbonyl iron (III) complexes.[12,14] Nevertheless the chemistry of iron-porphyrin carbonyl complexes has been studied in fair detail,[2] since there are many parallelisms in the behaviour of CO and O_2 in relation to natural systems such as haemoglobin, myoglobin, etc. By virtue of the ease of monitoring by means of infrared spectroscopy, the greater strength of the Fe–CO bond compared with Fe–O_2, and the absence of side processes, the reactions of both natural haems and their synthetic models with CO are widely used to elucidate the steric and electronic characteristics of these molecules. It has been established[37,38] that deuteriohaem and (TPP)Fe combine in succession with two CO molecules in inert solvents, but one of them is readily substituted on treatment with nucleophiles such as histidine, pyridine, etc. It has been established by X-ray diffraction that the Fe–C–O fragment in (TPP)Fe(CO)Py is linear and is arranged at right angles to the plane of the macroring,[39] while in the carbonylated natural haems the Fe–C–O angle is 135–145°.[40,41]

The ruthenium-porphyrin carbonyl complex, to which the formula (TPP)Ru(CO)Cl had been attributed initially,[42] has been obtained by treating an ethanol solution of $RuCl_3$ with CO and H_2TPP. Subsequent investigations[43,44] showed that this compound, which is also formed when H_2TPP is refluxed with $[Ru(CO)_3Cl_2]_2$ or $Ru_3(CO)_{12}$ in organic acids or benzene, contains no chlorine atoms and its composition is in fact (TPP)RuCO (IX). Coordination-unsaturated complexes of type (IX) have also been obtained from H_2MP, H_2AEP, and H_2PrTPP. These are brick-red crystalline compounds, stable in air, whose infrared spectra contain one ν(CO) band at ~1940 cm^{-1}. In solutions complexes (IX) combine with one molecule of the electron-donating solvents to form unstable 1:1 adducts from which the compounds LRu(CO)L' (X), where L = MP, AEP, or PrTPP have been obtained on treatment with the nucleophiles L' = pyridine, 2-methylpyridine, and 4-t-butylpyridine. It has been established by ^1H NMR[44–48] that compounds (X) (L = PrTPP) are capable of undergoing readily the intermolecular exchange of the ligand L' for the free nuclecphile present in solutions. For L' = 3,5- and 4,5-dimethylpyridazine, an intramolecular interchange of the two positions of the coordinated L' was observed,[48] its rate being 20–85 times greater than the rate of the intermolecular exchange.



(X) M = Ru
(XI) M = Os

Reactions involving the substitution of the CO groups in complexes (IX) and (X) by other ligands have been hardly investigated. It has been established[49] that, when a solution of (MP)RuCO in benzene is treated with NO at room temperature, the dinitrosyl complex $(MP)Ru(NO)_2$ is formed in a quantitative yield. When an attempt was made to brominate (OEP)Ru(CO)Py in the presence of an excess of KCN, the ionic complex $K^+[(OEP)Ru(CN)_2]^-$ was obtained.[50] Irradiation of (AEP)Ru(CO)Py solutions in pyridine or benzene with visible or ultraviolet light led to the formation of the dimer $[(AEP)RuPy]_2$, which the authors believe to contain the metal–metal double bond.[51]

Two communications concerning the X-ray diffraction analysis of the product of the reaction $Ru_3(CO)_{12}$ with H_2TPP have been published. The first of these,[52] in which the compound is described as a dicarbonyl complex (TPP).$Ru(CO)_2$ with non-linear Ru–C–O groups (with an Ru–C–O angle of 153.3°) and very long Ru–C distances (2.04 Å), is probably wrong. In the second communication,[53] the structure (X), where L' = EtOH, was attributed to the same complex recrystallised beforehand from a $CHCl_3$ – EtOH mixture. According to the former data,[52] the ruthenium atom is at the centre of the porphyrin macroring, the distance between the Ru atom and the oxygen atom of the coordinated ethanol molecule is 2.21 Å, the Ru–C bond length is 1.77 Å, and the Ru–C–O angle is 180°.

Similar parameters of the Ru–CO fragment have been observed also for the crystal structure of the complex (TPP)Ru(CO)Py,[53,54] but in this compound the Ru atom is displaced from the plane of the porphyrin macroring by 0.079 Å in the direction of the CO group.

At pH close to 7 the complex (MP)RuCO forms a 1:1 adduct with apomyoglobin. The study of the ultraviolet and visible spectra of this adduct led to the hypothesis that the distal histidine of apomyoglobin interacts with the Ru–CO group, deflecting the carbonyl group from the axis perpendicular to the plane of the porphyrin ring.[55] An analogous effect has been observed in the ruthenium carbonyl complex of the natural myoglobin.[56]

A brick-red dicarbonyl complex $(OEP)Ru(CO)_2$ has been obtained in a quantitative yield by treating benzene solutions of (OEP)Ru(CO)THF) or (OEP)Ru(CO)(EtOH) with CO. Analogous compounds have been obtained from H_2TPP and its derivatives containing the isopropyl or trifluoromethyl groups in the *para*-positions in the benzene rings. All

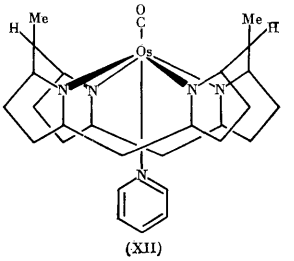
these compounds readily split off one CO molecule on storage or treatment with nucleophiles, for example, t-butylpyridine. As was to be expected, the ν(CO) band in the infrared spectra of the dicarbonyl complexes is at a much higher frequency (~1990 cm^{-1}) than in the spectra of compounds (IX) and (X) (~1940 cm^{-1}).[57]

The compounds (OEP)Ru(CO)(SR), where R = Et, CMe_3, or $CH_2CH_2CO_2Me$, which are possible models of the product of the addition of the CO group to the reduced cytochrome P 450, have been obtained by the reaction of (OEP)RuCO with mercaptide anions. The observed decrease of the ν(CO) frequency in the infrared spectra by 30 cm^{-1} and the upfield shift of the signals in the ^1H NMR spectra compared with complexes (IX) permit the conclusion that there is charge transfer from the negatively charged thiolate group to the Ru atom and (or) the porphyrin macroring.[58]

The osmium monocarbonyl complexes (XI) are much more stable than their iron and ruthenium analogues. They are formed when OsO_4 and H_2OEP are heated above 200 °C in the monomethyl ether of diethylene glycol with subsequent addition of nucleophiles L' [59] or on treatment of (OEP)OsPy with CO.[60] The complexes (OEP)Os(CO)L'(L' = MeOH, EtOH, THF, Py, PPh_3, or $AsPh_3$) are red or violet crystalline substances, stable in air, and comparatively stable in solutions. The ν(CO) frequencies in their infrared spectra increase from 1897 cm^{-1} for L' = THF to 1926 cm^{-1} for L' = PPh_3, which indicates a decrease of the strength of the M–CO bond with increasing π-acceptor capacity of the substituent L'. When compound (XI, L' = Py) is treated with the stronger π-acceptor $P(OMe)_3$, both pyridine and CO are substituted and (OEP)Os$[P(OMe)_3]_2$ is formed.

Comparison of the ν(CO) frequencies of the carbonyl pyridine complexes of metals of the iron triad (OEP)M(CO)Py, namely 1902 cm^{-1} for M = Os, 1932 cm^{-1} for M = Ru, and 1970 cm^{-1} for M = Fe, demonstrate unambiguously an increase of the capacity of the metal atom for the reverse transfer of electron density to the CO group in the sequence Fe < Ru < Os. These data agree well with the increase of the thermal stability of the complexes in the same sequence.

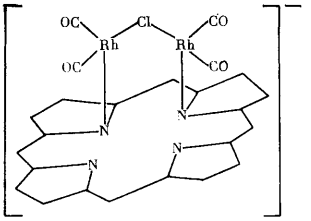
The electrochemical oxidation of the complex (XI, L' = Py) leads to the formation of the cation $[(OEP)Os(CO)Py]^+$ in which the presence of the Os^{3+} species has been postulated.[61] The reduction of this compound with sodioanthracene in THF does not entail a change in the oxidation state of the metal atom: after the addition of MeI to the reduced solution, the complex (XII), containing, according to X-ray diffraction data, a non-planar tetrapyrrole ligand (the angle of inflection along the axis passing through the sp^3-hybridised C atoms is 142°), was isolated. The Os atom lies 0.18 Å above the plane of the four pyrrole nitrogen atoms. The decrease of the ν(CO) frequency to 1963 cm^{-1} in the infrared spectrum of compound (XII) is probably associated with the decrease of the reverse electron donation by the metal atom to the orbital of the non-conjugated dimethylporphyrin ligand.[62]



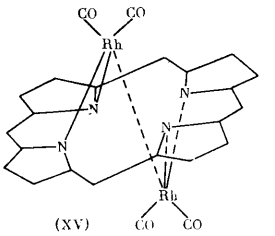
(XII)

The structure of the porphyrin complexes of rhodium depends greatly both on the reaction conditions and on the nature of the porphyrin. The reaction of $[Rh(CO)_2Cl]_2$ and H_2TPP in boiling benzene yielded the monocarbonyl complex (TPP)Rh(CO)Cl (XIII) and the σ-phenyl compound (TPP)Rh(Ph)Cl;[42,63] only a non-carbonyl product is formed in acetic acid.[64] The complex (XIII) is also obtained on treatment of (TPP)RhCl with CO under mild conditions (25 °C, 1 atm).[65]

In benzene at 20 °C H_2OEP reacts with $[Rh(CO)_2Cl]_2$ to form a dark-green product, to which the formula $H^+[(OEP).Rh_2(CO)_4Cl]^-$ (XIV) [ν(CO): 2045, 2035, 1983, and 1950 cm^{-1}] was attributed on the basis of spectroscopic data.[66] Complex (XIV) is comparatively unstable and is readily oxidised in air, being converted into the red (OEP).RhCl.$2H_2O$. In CH_2Cl_2 compound (XIV) splits off HCl and forms the neutral bimetallic product (OEP)$[Rh(CO)_2]_2$ (XV).[67,68] X-Ray diffraction analysis of compound (XV) showed that it contains two $Rh(CO)_2$ groups each of which is linked to two nitrogen atoms located on different sides of the macroring; the short metal–metal distance (3.094 Å) suggests the occurrence of interaction between the metal atoms via the aperture in the macroring.[69]

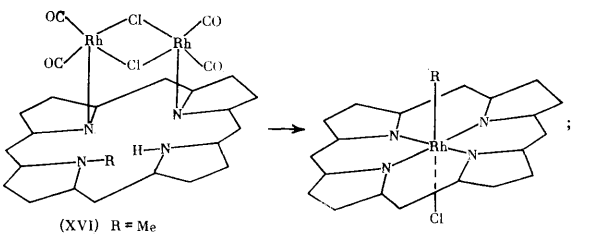


(XIV)



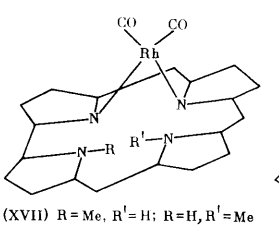
(XV)

Treatment of MeHOEP with $[Rh(CO)_2Cl]_2$ in benzene results in the formation of the dark-violet (MeHOEP) $[Rh(CO)_2Cl]_2$ (XVI) [ν(CO): 2075, 2050, 2010, and 1980 cm^{-1}].[70] Slight heating of compound (XVI) in $CHCl_3$ or its chromatography on a Al_2O_3 column entail a profound rearrangement of the molecule accompanied by the migration of the alkyl group to the Rh atom and the formation of the non-carbonyl complex $(OEP)Rh(CH)_3Cl$. The analogous reaction of rhodium carbonyl chloride with EtHOEP immediately results in the formation of (OEP)Rh(Et)Cl.

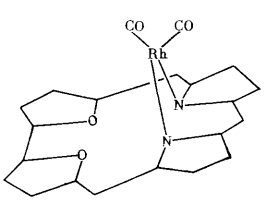


(XVI) R = Me

The reactions of $[Rh(CO)_2Cl]_2$ with corrole and dioxacorrole yielded the neutral monometallic complexes (XVII) and (XVIII) in which the macrorings play the role of bidentate four-electron ligands. It has been suggested that complexes of this type can be used as models of vitamin B_{12}.[71]



(XVII) R = Me, R' = H; R = H, R' = Me



(XVIII)

The stable monocarbonyl complexes LIr(CO)Cl have been obtained by the reactions of H_2L (L = MP or HeP) with π-olefin derivatives of iridium in alcoholic solutions or with $[Ir(CO)_3Cl]_2$ in acetic acid.[68,72] The CO group [ν(CO) ≅ 2060 cm^{-1}] is retained when these compounds are acted upon by pyridine, acids, and dilute solutions of alkalis; the dissociation of the Ir–CO bond, accompanied by a change in the oxidation state of the Ir atom, occurs only after prolonged heating of the complexes or on treatment with $NaBH_4$ or concentrated solutions of alkalis.

The bimetallic complex (OEP)$[Ir(CO)_3]_2$ (XIX) has been obtained by the reaction of $[Ir(CO)_3Cl]_2$ with H_2OEP in benzene. Its structure is probably analogous to that of the rhenium complex (II). The bis(chlorotricarbonyliridium) complex (MeHOEP)$[Ir(CO)_3Cl]_2$ (XX), whose structure is apparently close to that of compound (XIV), is formed from MeHOEP under the same conditions. When compound (XIX) is refluxed in $CHCl_3$, the monocarbonyl complex (OEP)Ir.(CO)Cl is obtained, while compound (XX) is converted into the σ-methyl derivative (OEP)$Ir(CH_3)Cl$.[73]

Thus the study of the metal–porphyrin carbonyl complexes revealed many previously unknown characteristic features of porphyrin macrorings:

1) A high capacity for coordination, which makes it possible to obtain stable bi- and tri-metal complexes in which the porphyrin functions as a hexa- and octa-dentate ligand.

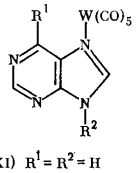
2) Stereochemical non-rigidity and the ability of the substituents at the pyrrole nitrogen atoms both to migrate between the pyrrole rings and to be transferred to the metal atom.

3) The ability of the π-electron system of the porphyrin not only to interact actively with the *d* orbitals of the metal atom at the centre of the macroring but also to form bonds with metal atoms located at a considerable distance from the plane of the porphyrin.

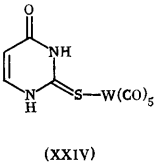
III. COMPLEXES OF METAL CARBONYLS WITH NUCLEIC BASES AND NUCLEOSIDES

Nucleic bases and nucleosides HL react with derivatives of metal carbonyls to form stable complexes in which they are usually linked to the metal atom via N → M donor–acceptor bonds.[74,75]

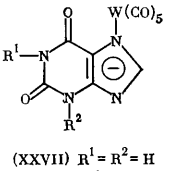
When $W(CO)_5$(THF) was acted upon by HL, neutral pentacarbonyl complexes $(OC)_5W(HL)$ (XXI–XXIV) were obtained. Reactions of this type also take place with the anions of nucleic bases. The charged complexes $[(OC)_5WL]^-$, isolated in the form of salts with the Na^+ or Ph_4As^+ cations [compounds (XXV)–(XXIX)], are formed in such cases. On the basis of spectroscopic data (Table 1), it has been established that adenine and adenosine are coordinated to the metal atom via a nitrogen atom in the five-membered heterocycle and not via the amino-group. An analogous coordination has been suggested for purine, theophylline and xanthine derivatives, while in the thiouracil complexes (XXIV) and (XXIX) the base is linked to the metal atom via an S–W bond.[74]



(XXI) $R^1 = R^2 = H$
(XXII) $R^1 = NH_2$, $R^2 = H$
(XXIII) $R^1 = NH_2$, R^2 = ribose



(XXIV)



(XXVII) $R^1 = R^2 = H$
(XXVIII) $R^1 = R^2 = Me$

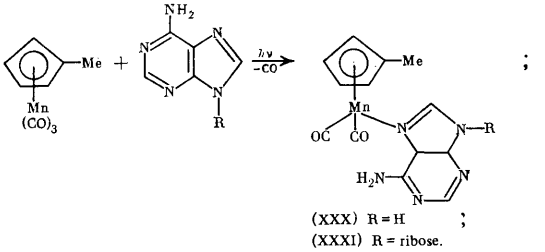
Analysis of the infrared spectra of complexes (XXI)–(XXIII) in the region of ν(CO) vibrations shows that, in terms of their donor–acceptor properties, the nucleic bases are close to nitrogen-containing Lewis bases such as pyridine.[76] There is virtually no difference between the type *E* frequencies of the neutral complexes (XXI) and (XXII), on the one hand, and the ionic complexes (XXV) and (XXVIII), on the other, which unambiguously demonstrates the delocalisation of the negative charge over the organic part of the complex anion. At the same time the slightly lower ν(CO) frequencies of type A_1 in the infrared spectra of the ionic complexes indicate a partial transfer of electron density from the herterocycle to the d_π orbitals of the tungsten atom.

Table 1. Parameters of the infrared spectra [in $CHCL_3$, ν(cm^{-1})] of complexes of tungsten carbonyl with nucleic bases and nucleosides.[74,75]

Compound	Base LH	C≡O			C=O	NH_2
		$A_1^{(1)}$	*E*	$A_1^{(2)}$		
Neutral compounds $(CO)_5W(LH)$						
(XXI)	purine	2073	1930	1895	—	—
(XXII)	adenine	2072	1925	1890	—	3445, 3410
(XXIII)	adenosine	2075	1933	1890	—	3420
(XXIV)	2-thiouracil	2075	1940	1800	1680	—
Ionic complexes $Na^+[(CO)_5WL]^-$						
(XXV)	purine	2064	1932	1884	—	—
(XXVI)	adenine	2060	1925	1880	—	3450, 3380
(XXVII)	theophylline*	2065	1925	1880	1638	—
(XXVIII)	xanthine*	2066	1932	1883	1690	—
(XXIX)	2-thiouracil*	2065	1922	1870	1661	—

*in ethanol.

The ethylenediamine complex of molybdenum *cis*-$Mo(CO)_4$(en) reacts with adenine, guanine, and theophylline salts at 110 °C with substitution of one CO group and the formation of the ionic complexes $K^+[Mo(CO)_3(en)L]^-$. The CO group is also substituted in the photochemical reactions of $(\eta^5\text{-}MeC_5H_4)Mn(CO)_3$ with adenine and adenosine:[74]

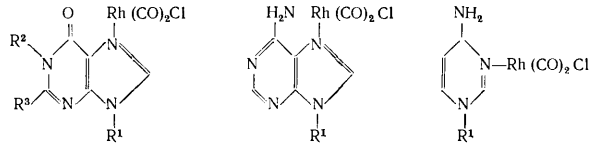


(XXX) R = H ;
(XXXI) R = ribose.

The higher ν(CO) frequencies in the infrared spectrum of the nucleoside complex (XXXI) (1910 and 1832 cm^{-1}) compared with the nucleic base complex (XXX) (1895 and 1825 cm^{-1}) indicate the electron-accepting character of the ribose fragment. An analogous conclusion can be reached from the comparison of the ν(CO) frequencies of the tungsten complexes (XXIII)–(XXII) (see Table 1).

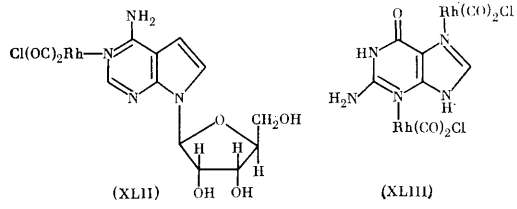
The dinuclear rhodium carbonyl chloride $[Rh(CO)_2Cl]_2$ reacts with nucleic bases with the opening of the chloride bridges and the formation of the monometallic complexes

$(OC)_2RhCl(HL)$ (XXXII)–(XLI), of which the infrared spectroscopic parameters are given in Table 2.[75]



(XXXII)–(XXXVII) (XXXVIII) (XXXIX)–(XLI)

Complex (XLII) with $\nu(CO)$ = 2075 and 2000 cm^{-1} has been obtained by the reaction of $[Rh(CO)_2Cl]_2$ with 7-desaza-adenosine (tubercidine). The reaction with guanine leads to the formation of the bimetallic complex having $\nu(CO)$ = 2103, 2080, 2040, 2012, and 2000 cm^{-1}, for which the structure (XLIII), having two independent $Rh(CO)_2Cl$ groups linked to the imidazole and pyrimidine nitrogen atoms, has been proposed.[75]



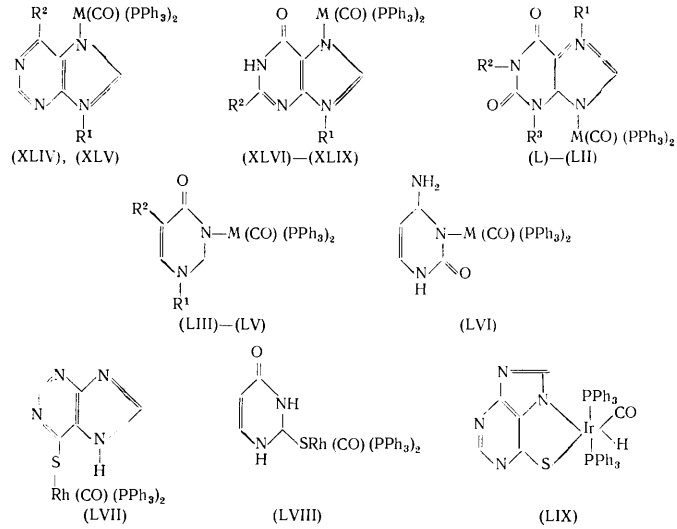
(XLII) (XLIII)

Table 2. Parameters of the infrared spectra (in ethanol) of complexes of the type $ClRh(CO)_2(LH)$.[75]

Compound	Base				$\nu(CO)$, cm^{-1}
	LH	R^1	R^2	R^3	
(XXXII)	hypoxanthine	H	H	H	2083, 2010
(XXXIII)	9-methylguanine*	Me	H	NH_2	2065, 1985
(XXXIV)	inosine	ribose	H	H	2085, 2015
(XXXV)	guanosine	ribose	H	NH_2	2084, 2013
(XXXVI)	1-methylguanosine*	ribose	Me	NH_2	2065, 1983
(XXXVII)	2',3'-*O*-isopropylideneguanosine**	2', 3'-*O*-isopropylideneribose	H	NH_2	2088, 2016
(XXXVIII)	adenosine	ribose	—	—	2074, 2017
(XXXIX)	cytosine	H	—	—	2082, 2010
	methylcytosine	Me	—	—	2083, 2010
	cytidine	ribose	—	—	2084, 2010

*in DMSO.
**in $CHCl_3$.

In the reactions with $ClM(CO)(PPh_3)_2$ (M = Rh or Ir), the anions of nucleic bases and nucleosides L^- behave as one electron ligands, substituting the chlorine atom and forming the neutral complexes $M(CO)(PPh_3)_2L$ (XLIV)–(LVI), whose properties are listed in Table 3.[74] In contrast to the rhodium complexes, the iridium compounds are more reactive and form adducts with oxygen both in solutions and in the crystalline state.



(XLIV), (XLV) (XLVI)–(XLIX) (L)–(LII)

(LIII)–(LV) (LVI)

(LVII) (LVIII) (LIX)

Table 3. Parameters of the infrared spectra (in $CHCl_3$) of compounds of the type $M(Co)(PPh_3)_2L$.[74]

Compound	Base				$\nu(CO)$, cm^{-1}	
	LH	R^1	R^2	R^3	M = Rh	M = Ir
(XLIV)	purine	H	H	—	1992	1980
(XLV)	adenine	H	NH_2	—	1990	1978
(XLVI)	hypoxanthine	H	H	—	—	1975
(XLVII)	inosine	ribose	H	—	1985	1974
(XLVIII)	guanine	H	NH_2	—	1976	1962
(XLIX)	guanosine	ribose	NH_2	—	1985	1974
(L)	xanthine	H	H	H	1989	1977
(LI)	theophylline	H	Me	Me	1987	1975
(LII)	theobromine	Me	H	Me	1973	—
(LIII)	uracil	H	H	—	1985	1971
(LIV)	uridine	ribose	H	—	1975	1965
(LV)	thymine	H	Me	—	1983	1967
(LVI)	cytosine	—	—	—	1981	1967

The complexes $Rh(CO)(PPh_3)_2L$ (LVII) [$\nu(CO)$ = 1986 cm^{-1}] and (LVIII) [$\nu(CO)$ = 1983 cm^{-1}], in which the anions of nucleic bases add to the metal atom via the sulphur atom, have been obtained by treating $ClRh(CO)(PPh_3)_2$ with potassium 6-mercaptopurinate and 2-thiouracil respectively. The metal hydride complex $HIr(CO)(PPh_3)_2L$ (LIX) with $\nu(CO)$ = 2047 cm^{-1} and $\nu(IrH)$ = 2155 cm^{-1}, in which the dianion of 6-mercaptopurine is apparently a two-electron chelate ligand, has been obtained by the reaction of potassium 6-mercaptopurinate with Vaska's complex $ClIr(CO).(PPh_3)_2$. In a neutral medium two 6-mercaptopurine molecules add to Vaska's complex and $HIr(CO)(PPh_3)_2L_2$ (LX) [$\nu(CO)$ = 2055 cm^{-1}, $\nu(IrH)$ = 2180 cm^{-1}], from which one molecule of the nucleic base is split off on treatment with KOH, the complex being converted into compound (LIX). The reaction of $ClIr(CO)(PPh_3)_2$ with 2-thiouracil yielded the complex (LXI), the infrared spectrum of which contains two $\nu(CO)$ bands at 2055 and 2034 cm^{-1}.[74] Judging from the high $\nu(CO)$ frequencies, this compound is also a hydride, i.e. $HIr(CO)(PPh_3)_2$, and the presence of two $\nu(CO)$ bands in the infrared spectra is probably associated with the formation of various isomers of compound (LXI) in the course of the reaction.

In conclusion of this Section, one may note that, despite the fact that the data available at present are limited, the use of metal carbonyl complexes has proved useful in securing

additional information about the active centres of purine and pyrimidine bases involved and about the electronic donor–acceptor properties of the monomeric fragments of nucleic acids.

IV. METAL CARBONYL COMPLEXES WITH AMINOACID AND PEPTIDE LIGANDS

Metal complexes of aminoacids and peptides have served for more than 100 years as models of the products of the reactions of metals with proteins and as models of biological systems in which the properties of proteins have been modified by the addition of metal atoms to them.[2,77,78] The synthesis and study of the properties of organometallic compounds containing aminoacid and peptide ligands opens up new possibilities for the determination of the mechanism of the interaction of protein systems with transition metal atoms.[79,80]

Three types of metal carbonyl derivatives incorporating aminoacids and peptide fragments are known at the present time:

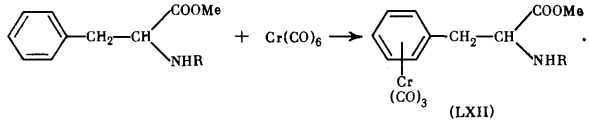
1) π-Complexes based on aminoacids and peptides.

2) Compounds formed as a result of the condensation of aminoacids with the ligand at the metal atom.

3) Metal carbonyl complexes formed as a result of the coordination of the metal atom to the functional groups of aminoacids and peptides.

1. π-Complexes Based on Aminoacids and Peptides

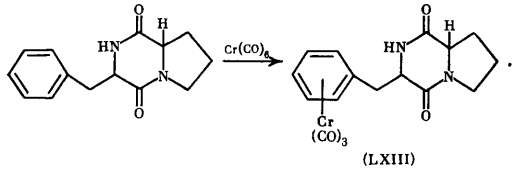
Aminoacids and peptides whose side chains incorporate an organometallic fragment belong to compounds of this class. It has been established recently[81] that derivatives of aromatic aminoacids with protected carboxy- and amino-groups readily react with chromium hexacarbonyl in ethereal or water-tetrahydrofuran media, forming the corresponding η^6-arene-chromium tricarbonyl complexes:



(LXII)

Derivatives of phenylalanine (LXII) are thermally unstable: R = CHO, m.p. 90 °C; R = CMeO, m.p. 99 °C; R = C(t-Bu)O, m.p. 130 °C. The analogous reactions with tryptophan and tyrosine derivatives lead to the formation of less stable compounds.

Stable π-complexes (LXIII) have been obtained by the reactions of $Cr(CO)_6$ with diastereoisomeric cyclic peptides whose composition includes a phenylalaninate fragment, no racemisation of the peptides being observed in the course of the reactions.



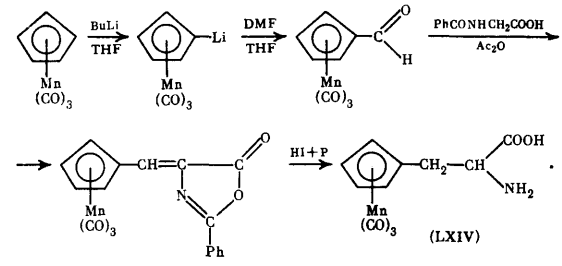
(LXIII)

LL, $[\alpha]_D$ -73.6° LL, $[\alpha]_D$ -90.4°, m.p. 228°

LD, $[\alpha]_D$ +51.2° LD, $[\alpha]_D$ +57.6°, m.p. 218°

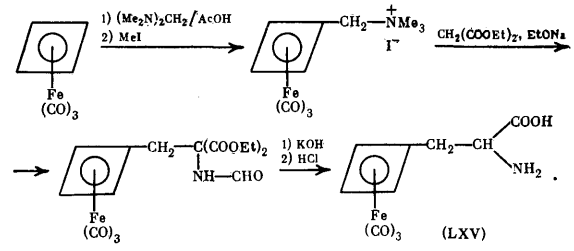
The formation reactions of the π-arene derivatives of metal carbonyls can probably serve as a good test of the presence of aromatic rings in various natural products.

Organometallic aminoacids can be obtained also directly from the corresponding π-complexes of transition metals. Thus cymantrenylalanine (LXIV) has been synthesised from η^5-cyclopentadienylmanganese tricarbonyl in 60% yield (m.p. 230 °C):[82]



(LXIV)

Another method has been used[82] to obtain (η^4-cyclobutadienylalanine)iron tricarbonyl (LXV) in 30% yield (m.p. 220 °C, with decomposition):

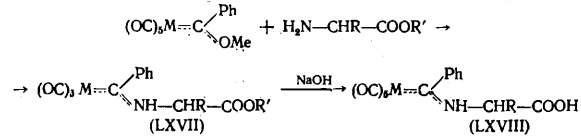


(LXV)

The properties of metal carbonyl aminoacids are apparently close to those of the usual aromatic aminoacids. It had been established earlier that the non-carbonyl analogue of these compounds, namely ferrocenylalanine $(\eta^5\text{-}C_5H_5)Fe[\eta^5\text{-}C_5H_4.CH_2CH(NH_2)COOH]$ (LXVI), which has been synthesised by a method[83] close to that used for the synthesis of compound (LXV), behaves in many reactions in the same way as phenylalanine. It enters into metabolic hydroxylation reactions and reactions involving coupling to glucuronic acid[84,85] and it can participate in peptide synthesis reactions.[86] Compound (LXVI) has been inserted in natural peptides such as encephalin and bradykinin.[82,87] The arene complexes of transition metal carbonyls are similar in many respects to ferrocene derivatives, but, by virtue of the presence of the M–CO groups in the molecules, it is much easier to follow the behaviour of these compounds in various processes. It therefore appears useful to employ metal carbonyl aminoacids as labels in protein molecules.

2. Compounds Formed as a Result of the Condensation of Aminoacids with the Ligand at the Metal Atom

Among compounds of this type, the carbene derivatives of Group VI metal pentacarbonyls, obtained by Fischer and Weiss[88–90] as a result of the condensation of aminoacid esters with phenyl(methoxy)carbene-chromium and tungsten pentacarbonyls have been most thoroughly investigated:



(LXVII) (LXVIII)

The complexes are formed readily at 20 °C in ether. Compounds (LXVII) and (LXIII) are readily fusible crystalline or oily substances, stable in air, and readily soluble in

polar organic solvents (Table 4). The ester groups in compounds (LXVII) are readily hydrolysed on treatment with alkalis and the acids (LXVIII) formed can participate in peptide synthesis reactions. A series of consecutive reactions involving the condensation of compound (LXVIII) with aminoacid esters in the presence of *N*-hydroxysuccinimide and dicyclohexylcarbodiimide yielded di-, tri-, and tetrapeptide complexes, which decompose on treatment with CF_3COOH at room temperature with liberation of the free peptide:

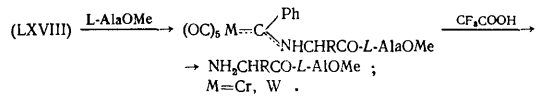
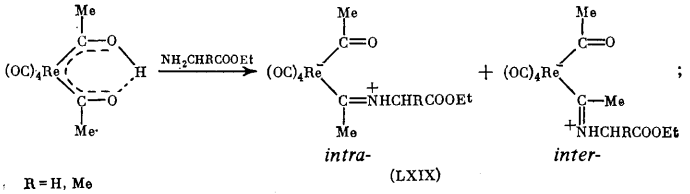


Table 4. Aminoacid – and peptide – carbene complexes of Group VI metals of the type $(OC)_5M[C(Ph)(NHCHRCOX)]$.[80–90]

NHCHRCOX	Yield, %	M.p., °C	$[\alpha]_{589}^{20}$, °
	M = Cr		
GlyOH	79	106—109	—
GlyOMe	66	55—72*	—
ClyOEt	97	—	—
L-AlaOH	87	77—82	+16
L-AlaOMe	87	87—88*	+13
L-ValOMe	70	75—78	—94
L-MetOMe	92	70—74	—77
L-SerOMe	76	135—145*	—35
L-PheOMe	87	—	—
L-ProOMe	78	86—89	—63
L-Glu(OMe)2	94	113—115	—95
Gly-GlyOH	98	120*	—
Gly-GlyOMe	67	105—106	—
L-Ala-L-AlaOMe	79	93—104*	—15
L-Leu-L-LeuOMe	82	143—145*	—98
L-Ala-L-Ala-L-AlaOMe	82	120*	—50
L-Ala-L-Ala-L-Ala-L-ProOMe	63	82—86	—48
Gly-L-Ala-L-Pro-GlyOMe	79	103—108*	—50
	M = W		
GlyOH	86	113—115*	—
GlyOMe	63	70—73	—
L-LeuOMe	77	86—108*	—52
Gly-L-ValOMe	75	139—145*	—22

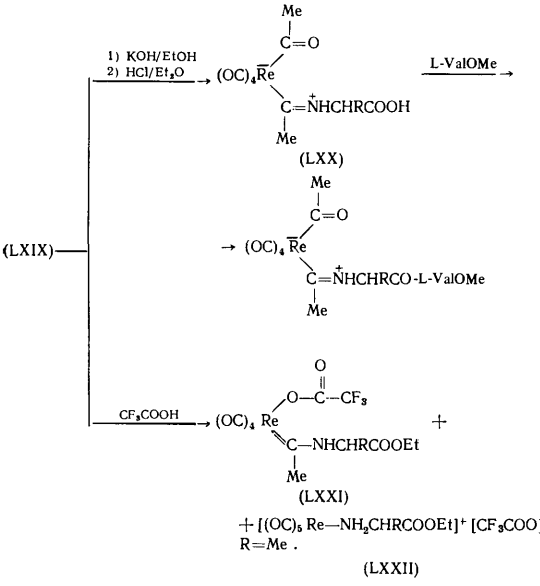
*With decomposition.

The organorhenium analogue of acetylacetone, namely tetracarbonyl rhena-acetylacetone, reacts with aminoacid esters in CH_2Cl_2 to form the isomers of the corresponding dipolar complexes (LXIX):



R = H, Me

The crystal structure of the *inter*-isomer (LXIX, R = H) is illustrated in Fig. 1. Hydrolysis of compound (LXIX) leads to the formation of the corresponding acids (LXX), which are capable of participating in subsequent condensation reactions with aminoacid esters. Complexes (LXIX) and (LXX) are much more stable than the related chromium and tungsten complexes (LXVII) and (LXVIII). When compound (LXIX) is acted upon by CF_3COOH, the neutral carbene complex (LXXI) and the ionic complex (LXXII), in which an ethyl alaninate molecule is coordinated to the metal atom via the amino-group, are formed:[91]



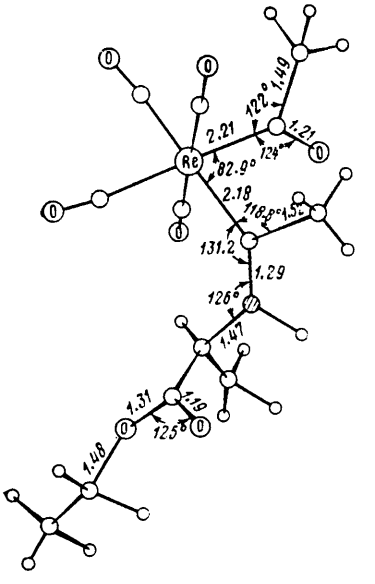
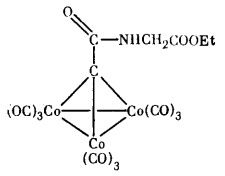


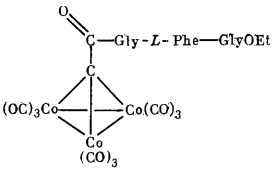
Figure 1. The structure of *inter*, *cis*-$(OC)_4Re[C(O)Me]$. $.[C(Me)(L\text{-}AlaOEt)]$.[91]

Instances of the addition of aminoacids and peptides to transition metal cluster compounds containing an active carbon atom are known. When the ionic complex $[(CO)_9$. $.Co_3CCO] + [PF_6]^-$ was allowed to react with ethyl glycinate in CH_2Cl_2, the neutral carbamide derivative (LXXIII), melting at 117 °C, was obtained. The tripeptide complex

(LXXIV) has been synthesised by an analogous reaction.[92]

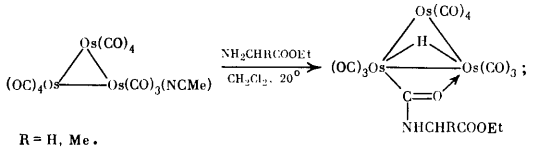


(LXXIII)



(LXXIV)

The chiral carbamide complexes (LXXV) have been obtained by the reaction of $Os_3(CO)_{11}(NCMe)$ with glycine and alanine esters.[93]



R = H, Me.

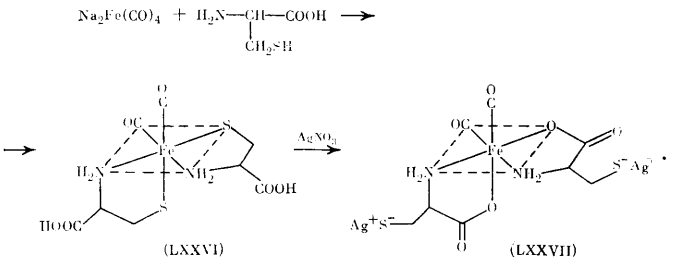
(LXXV)

With the aid of aminoacid esters deuteriated at the nitrogen atom, it has been established that the hydride bridge in compound (LXXV) is formed as a result of hydrogen transfer from the amino-group.

3. Metal Carbonyl Complexes Formed as a Result of the Coordination of the Metal Atom to Functional Groups in Aminoacids and Peptides

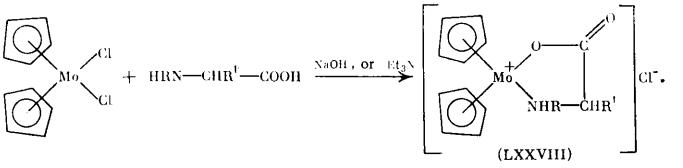
Complexes in which the aminoacid fragments are directly linked via their functional groups to the metal atom constitute the most thoroughly investigated class of organometallic aminoacid derivatives. In these compounds the aminoacids can behave as either monodentate one-electron (for coordination to the carboxyl oxygen) or two-electron (for coordination to the amino-group substituents) or as three-electron chelate or bridging ligands. The functional groups of aminoacids are coordinated to metal atoms comparatively readily and the problem of the synthesis of organometallic aminoacid complexes reduces mainly to the problem of the solvent in which both the aminoacids and the initial organometallic compounds are equally readily soluble.

The first aminoacid metal carbonyl complex, namely dicysteinatoiron dicarbonyl, was synthesised as early as 1933,[94] but its structure was not established until the end of the 1960's after detailed spectroscopic investigations.[95,96] The red crystalline product (LXXVI), obtained by the reaction of cysteine with $Na_2Fe(CO)_4$, contains chelating aminoacid ligands coordinated to the iron atom via the amino-group and the sulphur atom. The presence in the infrared spectrum of compound (LXXVI) of bands at 1717 and 1690 cm^{-1} indicates the presence of free COOH groups in this complex. Treatment of solutions of compound (LXXVI) with silver salts leads to a rearrangement of the chelating ligands and the cysteinate groups in the resulting green complex (LXXVII) are linked to the iron atom via the nitrogen and oxygen atoms: ν(COO) = 1608 and 1417 cm^{-1}. The increase of the stretching vibration frequencies of the CO groups at the iron atom after the change in the coordination of the aminoacid ligand, i.e. ν(CO) = 2030 and 1978 cm^{-1} for compound (LXXVI) and 2050 and 1990 cm^{-1} for compound (LXXVII), unambigously demonstrates the more pronounced electron-accepting character of the carboxylate group compared with the sulphide group:



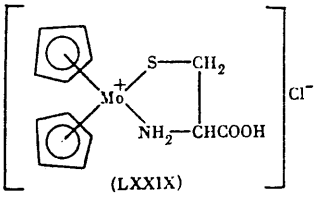
(LXXVI) (LXXVII)

The organometallic aminoacid complexes of molybdenum were first synthesised from dicyclopentadienylmolybdenum dichloride:[97]

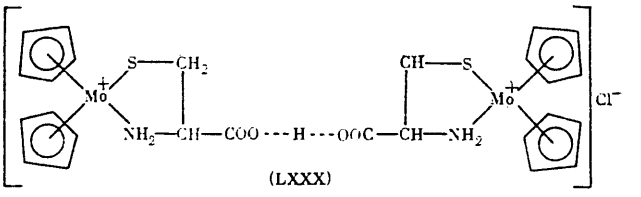


(LXXVIII)

where HRNCHR'CO = Gly, L-Ala, L-Phe, L-Val, L-Leu, L-Ile, L-Pro, L-Met, L-Ser, CH_3NHCH_2CO, or $CH_3NHCH_2.CH_2CO$. The complexes (LXXVIII) are crystalline substances stable in air and resistant to the action of strong acids. The study of the ^1H NMR spectra of these compounds showed that the hydrogen atoms at the α-carbon atoms readily exchange with D_2O in weakly alkaline solutions. When Cp_2MoCl_2 is treated with cysteine, two products are formed: the monomer (LXXIX) and the dimer (LXXX), in which the cysteinate ligands are coordinated to the molybdenum atom via the sulphide and amino-groups. The reaction of Cp_2MoCl_2 with cystine is accompanied by the dissociation of the S–S bonds and leads to the formation of compound (LXXIX).

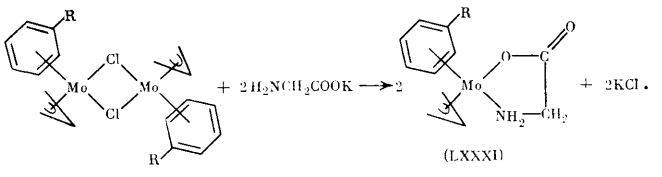


(LXXIX)



(LXXX)

The red crystalline glycinate complexes (LXXXI, R = H or Me) have been obtained by treating bis(η^6-benzene-η^3-allylmolybdenum chloride with potassium glycinate:[98]



(LXXXI)

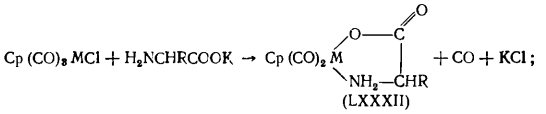
In contrast to the dicyclopentadienyl compounds (LXXVIII), the complexes (LXXXI) are decomposed by acids with liberation of propene.

Table 5. Aminoacid chelate complexes of molybdenum and tungsten.[99-101]

Compound	M.p., °C	ν(CO)	ν(COO)	ν(NH_2)	ν(OH)
$Cp(CO)_2Mo(GlyO)$	240	1965, 1864	1610	3224, 3110	—
$Cp(CO)_2Mo(SerO)$	210	1967, 1865	1630	3180	—
$Cp(CO)_2Mo(N,N\text{-}Me_2GlyO)$	205	1967, 1870	1660	—	—
$Cp(CO)_2Mo(L\text{-}AlaO)$	230	1964, 1865	1610	3220, 3110	—
$Cp(CO)_2Mo(L\text{-}2\text{-}MeAlaO)$	225	1963, 1865	1608	3223, 3132	—
$Cp(CO)_2Mo(L\text{-}ValO)$	235	1962, 1865	1630	3225, 3110	—
$Cp(CO)_2Mo(L\text{-}SerO)$	250	1965, 1865	1625	3270, 3140	3400
$Cp(CO)_2Mo(L\text{-}TryO)$	250	1965, 1865	1625	3280, 3220, 3105	3500
$Cp(CO)_2MO(D\text{-}TryO)$	250	1965, 1865	1625	3280, 3220, 3105	5300
$Cp(CO)_2Mo(L\text{-}HisO)$	190	1967, 1870	1615	3220, 3203	—
$Cp(CO)_2Mo(L\text{-}PheO)$	205	1965, 1865	1635	3220, 3105	—
$Cp(CO)_2Mo(L\text{-}N\text{-}PhCH_2PheO)$	175	1967, 1870	1632	3090	—
$Cp(CO)_2Mo(L\text{-}ProO)$	210	1963, 1865	1613	3145	—
$Cp(CO)_2Mo(D\text{-}ProO)$	210	1963, 1865	1613	3245	—
$Cp(CO)_2Mo(L\text{-}LysO)$	230	1965, 1865	1630	3220	—
$Cp(CO)_2Mo(L\text{-}GluO)$	150	1964, 1864	1630	3220, 3105	—
$Cp(CO)_2Mo(L\text{-}S\text{-}MeCysO)$	165	1967, 1867	1636	—	—
$Cp(CO)_2Mo(L\text{-}CysO)Li$	146	1947, 1850	1600	—	—
$Cp(CO)_2Mo(L\text{-}CysOMe)$	55*	1955, 1852	—	—	—
$Ind(CO)_2Mo(L\text{-}AlaO)$**	—	1965, 1870	1617	3210, 3110	—
$Cp(CO)_2W(SerO)$	209	1948, 1844	1640	3190, 3120	—
$Cp(CO)_2W(L\text{-}AlaO)$	240	1945, 1840	1620	3220, 3110	—
$(MeC_5H_4)(CO)_2W(L\text{-}AlaO)$	210	1942, 1840	1637	3220, 3133	—

*With decomposition.
**Ind = η^5-indenyl.

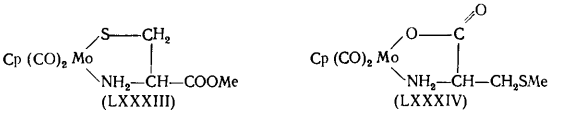
An analogous approach has been used to synthesise η^5-cyclopentadienyl-molybdenum and -tungsten dicarbonyl complexes with chelating aminoacid ligands:[99,100]



M=Mo, W

The complexes (LXXXII) (Table 5) are comparatively stable crystalline substances soluble in polar organic solvents. Since the metal atom in these compounds is chiral, the complexes exist in the form of two stereoisomers, which can be separated chromatographically. The structure of one of these complexes, established by X-ray diffraction, is illustrated in Fig. 2.

Cysteine and its methyl ester react with $Cp(CO)_3MoCl$ to form the complexes (LXXXIII) with a chelate N,S-ring, but the analogous reaction with *S*-methylcysteine leads to the formation of compound (LXXXIV) with the ligand coordinated via the N and O atoms.[100,101]



As for the iron cysteinate complexes (LXXVI) and (LXXVII), the infrared spectra of the molybdenum derivatives show a significant increase of the ν(CO) frequencies on passing from complexes with N,S-coordination of the ligand to the N,O-isomers: 1947 and 1850 cm^{-1} for compounds (LXXXIII) and 1967 and 1867 cm^{-1} for compounds (LXXXIV) respectively. Thus the type of coordination of the cysteinate fragment to the metal atom can be readily established on the basis of the infrared spectra of the carbonyl complexes in the ν(CO) region.

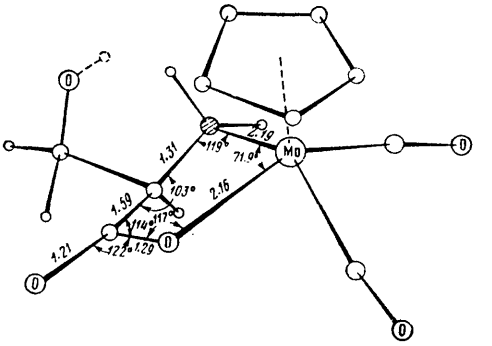
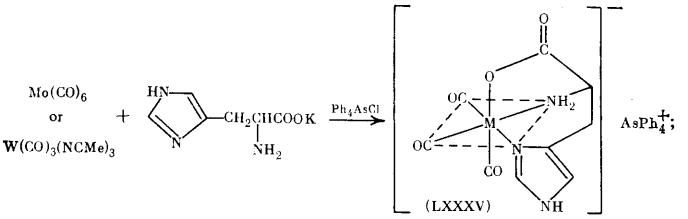
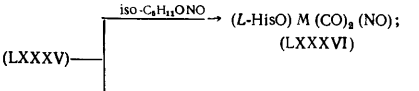


Figure 2. The structure of η^5-cyclopentadienyldicarbonyl-(L-serinato)molybdenum $Cp(CO)_2Mo(L\text{-}SerO)$.[100]

The reactions of $Mo(CO)_6$ or $W(CO)_3(NCMe)_3$ with potassium histidinate in alcoholic solutions lead to the formation of the ionic tricarbonyl complexes (LXXXV) in which the histidinate anion behaves as a five-electron tridentate ligand. By treating them with isopentyl nitrite or allyl bromide, it is possible to obtain the neutral dicarbonyl histidinate compounds (LXXXVI) and (LXXXVII) respectively:[102]



M = Mo, ν(CO) 1895, 1763, 1730 cm^{-1}; M = W, ν(CO) 1877, 1737 cm^{-1}.



(LXXXVI), M=Mo, ν(CO) 2014, 1913 cm^{-1}; (LXXXVII), M=Mo, ν(CO) 1937, 1846 cm^{-1}; M=W, ν(CO) 1927, 1837 cm^{-1}.

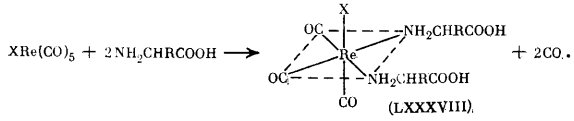
The tungsten pentacarbonyl complexes with aminoacid ligands linked to the metal atom only by the amino-group are relatively unstable. They can be obtained[103] by irradiating tungsten hexacarbonyl and aminoacid esters with ultraviolet light in non-polar solvents, for example:

$$W(CO)_6 + NH_2CHRCOOMe \xrightarrow[C_6H_6]{h\nu} (OC)_5W(NH_2CHRCOOMe) + CO;$$

R=CH_2CHMe_2, ν (CO) 2072, 1925 and 1893 cm^{-1}; ν (COO) 1738 cm^{-1}.

The dipeptide pentacarbonyl complex $(OC)_5W$-Gly-GlyOH, which decomposes on heating above 80 °C, has been obtained by the photochemical reaction between $W(CO)_6$ and glycylglycine.[103] In polar solvents, aminoacid compounds of the type $(OC)_5WL$ readily split off a ligand molecule.

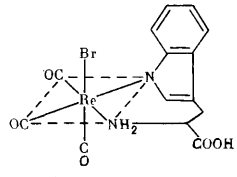
The reactions of aminoacids and their derivatives with rhenium carbonyl complexes have been studied in detail. When rhenium pentacarbonyl halides and α-aminoacids are refluxed in dioxan, stable bisaminoacid complexes (LXXXVIII) with a facial disposition of the non-carbonyl ligands at the metal atom are formed:[104–107]



(LXXXVIII)

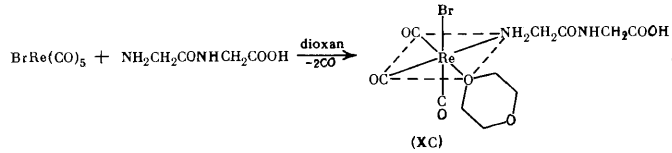
where $NH_2CHRCOOH$ = GlyOH, DL-AlaOH, DL-LeuOH, DL-ValOH, DL-β-Ph-α-AlaOH, or DL-β-2-thienyl-α-alanine. Compounds of the same type have been obtained with certain β-aminoacids: β-AlaOH, DL-β-Ph-β-AlaOH, and DL-β-2-thienyl-β-alanine.[104–107] The analogous manganese compounds are formed in the reactions of manganese carbonyl halides with GlyOH and AlaOH.[108] The study of the kinetics of the formation of the complexes (LXXXVIII) showed that the reaction proceeds preferentially via a dissociation mechanism and its rate is determined by the rate of dissociation of CO.

The monoaminoacid complex (LXXXIX), in which a tryptophan molecule is coordinated to the rhenium atom via both the amino-group and the indolyl nitrogen atom, has been obtained by the reaction of $BrRe(CO)_5$ with tryptophan.[106]



(LXXXIX)

The reactions of $BrRe(CO)_5$ with cysteine and threonine led to the formation of complexes of type (LXXXVIII), in which these potentially tridentate aminoacids are coordinated to the metal atom only via the amino-groups.[109] In the reaction of $BrRe(CO)_5$ with glycylglycine in boiling dioxan, two CO molecules are also evolved, but the resulting complex (XC) incorporates only one dipeptide molecule coordinated via the amino-group, while the other vacant site is occupied by a solvent molecule:[110,111]

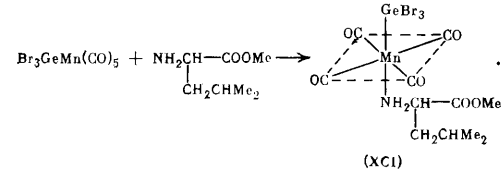


(XC)

The additional interaction between the peptide CONH group and the rhenium atom apparently plays a decisive role in stabilising complex (XC). The impossibility of the addition of a second glyglycine ligand to the metal atom can hardly be due to steric hindrance, because the more bulky β-indolylacetic acid gives rise to a disubstituted product of type (LXXXVIII) in an analogous reaction with $BrRe(CO)_5$.[107] The approach of a second dipeptide molecule to the rhenium atom in complex (XC) is apparently hindered by purely electrostatic factors.

The complexes (LXXXVIII)–(XC) are yellow oily or solid amorphous substances, which are resistant to the action of oxygen and water. At the same time they are hygroscopic and readily form solvates on reaction with both water and polar organic solvents such as dioxan, alcohols, acetone, etc. Aqueous solutions of the complexes give an acid response and can be titrated with alkalis. The infrared spectra of compounds (LXXXVIII)–(XC) in polar organic solvents show the absorption band due to the free COOH group in the range 1700–1730 cm^{-1} and three intense ν(CO) bands near 2030, 1910, and 1890 cm^{-1}, indicating a facial configuration of the CO groups linked to the rhenium atom.

The introduction of a strong π-acceptor substituent at the metal atom weakens the M–CO bond in the *trans*-position relative to the substituent and promotes the substitution of the carbonyl group by n-donor ligands. Thus, treatment of $Br_3GeMn(CO)_5$ by the methyl ester of leucine yielded the relatively unstable bimetallic complex (XCI) with the *trans*-configuration of the non-carbonyl ligands, the infrared spectrum of which contains ν(CO) bands, at 2082 and 2002 cm^{-1}, which are characteristic of the local D_{4h} symmetry of the $M(CO)_4$ group:[112]

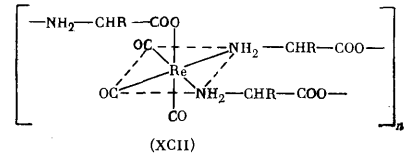


(XCI)

However, when the stannyl derivatives of rhenium carbonyl, namely $X_3SnRe(CO)_5$ (X = Cl or Br), are treated with aminoacid esters, the Sn–Re bond is ruptured and the disubstituted carbonyl halide complexes of type (LXXXVIII) are formed.[113] The reaction probably proceeds in such cases via the intermediate ionic complexes $[(OC)_5ReNH_2CHRCOOR']^+ . [SnX_3]^-$, resembling the complex (LXIX) examined above. A stable aminoacid compound with an Sn–Re bond has been obtained by the reaction of $SnCl_2$ with the bis(ethyl leucinate) derivative of rhenium carbonyl chloride:[113]

$$fac\text{-}ClRe(CO)_3[NH_2CH(CH_2CHMe_2)COOEt]_2 + SnCl_2 \rightarrow$$
$$\rightarrow fac\text{-}Cl_3SnRe(CO)_3[NH_2CH(CH_2CHMe_2)COOEt]_2.$$

In the interaction of salts of α-aminoacids with rhenium pentacarbonyl bromide or on treatment of solutions of the complexes (LXXXVIII) with KOH, the bromine atom is substituted and the polymeric compounds (XCII) are formed, in which the aminocarboxylate fragments function as bridges between the metal atoms:[104,114]

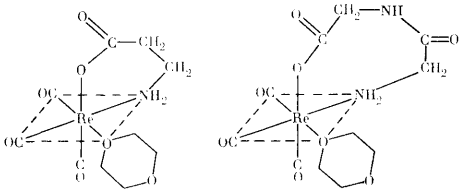


(XCII)

These are solid amorphous substances, which soften at 70–120 °C and are readily soluble in THF, $CHCl_3$, acetone, and alcohols. The cryoscopic determination of the molecular weight of the DL-α-phenylalaninate derivative, carried out in dioxan, showed that the number of units *n* in the polymer

molecule is close to four. The infrared spectra of the complexes (XCII) are analogous to those of compounds (LXXX-VIII), but, instead of the band due to the COOH group, they exhibit in the region of 1730 cm^{-1} bands associated with the vibrations of a bound COO group near 1650 and 1400 cm^{-1}.

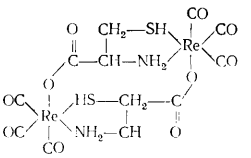
The reaction of $BrRe(CO)_5$ with salts of β-alanine and glycylglycine lead to the formation of the crystalline chelate complexes (XCIII) and (XCIV) respectively, which are sparingly soluble in organic solvents.[104,105,110,111]



(XCIII) (XCIV)

The complex (XCIII) is formed in polymers also on direct interaction between $BrRe(CO)_5$ and β-alanine in boiling dioxan. On the other hand, the reaction between $BrRe(CO)_5$ and salts of β-aminoacids containing an aromatic substituent (the phenyl or 2-thienyl group) at the β-carbon atom lead only to polymeric products of type (XCII).

Treatment of $BrRe(CO)_5$ with potassium DL-cysteinate yielded[109] a pale brick-red amorphous product (XCV), readily soluble in polar organic solvents. Solutions of this compound cannot be titrated with either alkalis or acids and the complex is inert with respect to nucleophiles. Determination of its molecular weight (by cryoscopy in dioxan) showed that it is a dimer. On the basis of these data as well as the analysis of the infrared spectra, it was suggested that all the functional groups of the aminoacid ligand in compound (XCV) are linked to the metal atom.

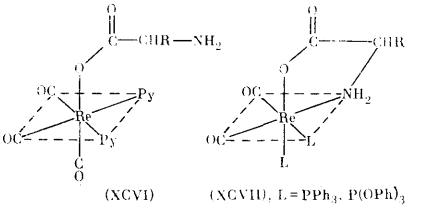


(XCV)

The analogous reaction of $BrRe(CO)_5$ with the potassium salt of DL-threonine gave rise to the colourless tetramer $\{(OC)_3ReNH_2CH[CH(Me)OH]COO\}_4$, whose solutions give an alkaline response. Probably not all the amino-groups in this compound are linked to the metal atoms.

The Re–N bonds in the aminoacid derivatives of rhenium carbonyl are comparatively weak and are readily ruptured in the presence of stronger Lewis bases L = Py, PPh_3, or $P(OR)_3$. Treatment of compounds of type (LXXXVIII) with L leads to the liberation of the free aminoacids and the formation of the complexes $BrRe(CO)_3L_2$, whose structure depends both on the nature of L and on the characteristics of the aminoacid ligands.[104,107,115] The reactions with pyridine in all cases give rise to *cis*-$BrRe(CO)_3(Py)_2$, while the reactions with $P(OPh)_3$ give rise to *trans*-$BrRe(CO)_3.[P(OPh)_3]_2$. The pathway followed in the reactions between compounds (LXXXVIII) and PPh_3 depends on the steric characteristics of the aminoacid ligands. When the complexes (LXXXVIII) with small aminoacid ligands such as glycine or β-alanine are acted upon by PPh_3, the product is *cis*-$BrRe(CO)_3(PPh_3)_2$, while the reactions with the complexes containing more bulky aminoacids, such as, for example, valine or leucine lead to *trans*-$BrRe(CO)_3(PPh_3)_2$. In the intermediate cases (α-alanine, β-phenyl-β-alanine, threonine) a mixture of the *cis*- and *trans*-isomers of $BrRe(CO)_3(PPh_3)_2$ was obtained. The sensitivity of the reactions of compounds (LXXXVIII) and PPh_3 to the steric effects of the aminoacid ligands is very great: the replacement of the phenyl group in β-phenyl-α-alanine by the 2-thienyl group alters the geometry of the substitution product. These results lead to the possibility of using aminoacid derivatives of metal carbonyls for the specific synthesis of complexes with a given structure.

The structure of the complexes formed when the polymeric compounds (XCII) are treated with nucleophiles also depends on the nature of L.[114,115] Pyridine ruptures the Re–N bond and the resulting mononuclear products (XCVI) contain an aminocarboxylate fragment coordinated to the metal atom only via the oxygen atom.

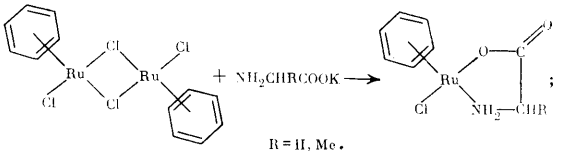


(XCVI) (XCVII), L = PPh_3, $P(OPh)_3$

The complexes (XCVI) are colourless crystalline substances melting above 200 °C and readily soluble in polar organic solvents and water. The aqueous solutions have an alkaline response and can be titrated with HCl. The infrared spectra are seen to contain three intense ν(CO) bands in the range 1900–2030 cm^{-1} and ν(COO) bands at 1645 and 1390 cm^{-1}. It was not possible to convert compounds (XCVI) into chelate complexes even by prolonged refluxing in dioxan.

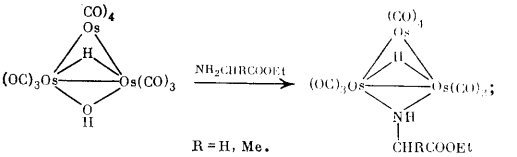
On the other hand, the reactions of compounds (XCII) with PPh_3 and $P(OPh)_3$, i.e. with nucleophiles exhibiting an appreciable π-acceptor capacity, lead to the formation of the chelate dicarbonyl complexes (XCVII)–crystalline products which are soluble in polar and organic solvents but are insoluble in water. Complexes of type (XCVII) with six-membered chelate rings have been obtained from compounds (XCII) having β-aminoacid ligands and also on treating $BrRe(CO)_3(NH_2CH_2CH_2COOH)_2$ with $P(OPh)_3$. The infrared spectra of all the complexes (XCVII) each show two ν(CO) bands at 1940 and 1860 cm^{-1} for L = PPh_3 or 1965 and 1880 cm^{-1} for L = $P(OPh)_3$ and ν(COO) bands at 1640 and 1400 cm^{-1}.[114]

The aminoacid derivatives of Group VIII metals have been less thoroughly investigated. The preparation of η^6-benzeneruthenium complexes with chelating glycinate and alaninate ligands has been reported:[116]



R = H, Me.

When $HOs_3(OH)(CO)_{10}$ is treated with the ethyl esters of glycine and α-alanine, compounds with an unusual imide bridge group are formed:[93,117]



R = H, Me.

A series of mononuclear crystalline dicarbonyl complexes with the chelating aminocarboxylate ligands $(OC)_2\overline{RhNHRCHR'COO}$ (XCVIII), where NHRCHR'COOH = GlyOH, L-AlaOH, β-AlaOH, DL- and L-LeuOH, L-HisOH, L-TyrOH, SerOH, DL- and L-PheOH, and p-$HOC_6H_4NHCH_2COOH$, have been obtained[118–120] by the reactions of aminoacids with the dinuclear rhodium carbonyl chloride $[Rh(CO)_2Cl]_2$ in benzene. It has been observed that these compounds readily react with tetracyanoethylene to form 1:1 adducts. The nucleophiles L, which consist of amines, 2,2'-bipyridyl, and o-phenanthroline, substitute both CO groups in the complexes (XCVIII), while treatment of the latter with L = PPh_3 or $AsPh_3$ in benzene or acetone entails the substitution of only one CO group and the formation of the monocarbonyl compounds $L(CO)\overline{RhNHRCHR'COO}$ (XCIX). The complexes (XCIX) can also be obtained by treating a mixture of $RhCl_3 . xH_2O$ and PPh_3 in benzene with aminoacids in an atmosphere of CO. The reactions of compounds (XCVIII) with PPh_3 in chloroform leads to the elimination of the aminoacid ligands and the formation of $[Rh(CO)(PPh_3)Cl]_2$ and an analogous result is obtained when gaseous HCl or HBr are passed over the solid complexes (XCIX). On the other hand, when gaseous chlorine is bubbled through a suspension of $(Ph_3P)(CO)\overline{RhNH_2CHR'COO}$ (R = H or Me) the bond between the aminoacid ligand and the metal is retained and an ionic complex is formed to which the composition $[Ph_3P)(CO).\overline{RhNH_2CR'ClCOO}]^{2+}.2Cl^-$ has been attributed.[120]

The data examined in this review show that aminoacids and their derivatives can form complexes having a wide variety of structures with transition metals in low oxidation states under comparatively similar conditions. By virtue of their ambident nature, the aminoacid fragments can function as terminal ligands coordinated to the metal atom via the N or O atoms, can participate in the formation of metallocycles, and finally can serve as bridges between two metal atoms. Arene π-complexes can be obtained from aromatic aminoacids. In all these reactions the metal atoms show a tendency to retain their 16- or 18-electron valence shell, which greatly facilitates the determination by spectroscopic methods of the structures of the complexes formed.

Derivatives of rhenium carbonyl, which exhibit an enhanced stability and contain numerous CO groups, some of which are retained under the conditions of the substitution reaction and which have a fixed octahedral configuration of the ligands around the metal atom, are especially convenient as model compounds for the study of the reactions of protein molecules with transition metal compounds. With the aid of these compounds, it has been possible to discover the importance of the steric features of the aminoacid ligands and their influence on the chemical properties of aminoacid complexes.

The formation of comparatively stable metal carbonyl aminoacid complexes and the possibility of a subsequent ready dissociation of the metal–nitrogen bonds on treatment with nucleophiles suggest the likely usefulness of the employment of the metal carbonyl groups for the protection of the amino-groups in the synthesis of peptides and in other reactions of biological compounds containing aminoacid fragments.

The possibilities inherent in the application of organometallic compounds in biochemistry are by no means exhausted by the examples quoted in this review. Reports have been published recently concerning the synthesis of metal carbonyl complexes with biological ligands such as vitamins,[121] monosaccharides,[122] steroids,[123] etc. Certain natural products, which are difficult to obtain otherwise, have been synthesised successfully with the aid of metal carbonyls, for example, one of the insect pheromones whose molecule includes the vinylallene group.[124]

There is no doubt that further development of bioorganometallic chemistry will make a significant contribution to our understanding of the role of metals in biological processes. Furthermore, studies in this field should provide a basis for a search for a new type of catalyst and for the development of fundamentally new technological processes, the conditions in which will be similar to those in reactions occurring in living organisms in the presence of metalloenzymes.

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The Macrokinetics and Rheokinetics of the Hardening of Oligomers

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The review deals with the investigation and phenomenological description of the macrokinetics of the hardening of reactive oligomers and the change in their rheological properties observed in the course of this process. Attention has been concentrated on the establishment of a relation between the macrokinetics and rheokinetics of the hardening process. The influence of deformation on the hardening kinetics is examined and the role of non-isothermal effects induced by various factors as well as the formulation of the hydrodynamic problems concerning the flow of liquids with variable rheological properties are discussed. The bibliography includes 143 references.

CONTENTS

I.	Introduction	293
II.	Changes in the relaxation states during hardening	293
III.	The macrokinetics of the hardening process	294
IV.	The rheology (rheokinetics) of the hardening process	298
V.	The flow of reactive oligomers	301

I. INTRODUCTION

The hardening of reactive oligomers (RO), i.e. the transition from the comparatively non-viscous liquid to a solid infusible material, is one of the principal technological processes associated with the chemistry of macromolecular compounds and is widely used in various branches of modern industry, including aerospace engineering, machine engineering, power engineering, etc. This process occurs in the manufacture of reinforced plastics of all types, plays an important role in the deposition of protective and insulating coatings, and recently has found application in the preparation of constructional components. The wide variety of the structures of RO and the possibility of their comparatively simple combination with various fillers and reinforcing elements are responsible not only for the extremely broad spectrum of the properties of the final products and articles made from them but also for different versions of the kinetics of the reactions occurring during the hardening of RO as well as the topology of the structures produced. Many problems associated with the chemistry of RO have been considered not only in hundreds of original communications but also in reviews.[1]

At the same time there exists an important aspect of the general problem of the investigation of the RO hardening processes which has so far been comparatively little reflected in the scientific literature, although there can be no doubt about its fundamental and technological importance. This concerns the general features of the time variation of the rheological properties of RO during the hardening process, so that there arises a single macro- and rheo-kinetic problem which involves the establishment of a correspondence between the macrokinetics of the hardening process and the change in the rheological properties of the RO as a consequence of this process. The terms "kinetorheology" or "rheokinetics", first proposed in 1976 [2] and then used in Soviet literature,[3] aptly reflect the range of processes which should be considered in studies on the kinetics of the variation of rheological properties; however, it is essential to establish a relation between the rheokinetics and macrokinetics of a chemical process.[4] Certain aspects of this problem, considered in the literature up to 1980, were dealt with in a previous review.[5] This review is devoted to a more detailed discussion of the problems associated with the macrokinetics and the rheokinetics of the hardening of oligomers; mainly the literature data of the last five years are considered.

The study of the rheokinetics of the hardening reactions of RO is of dual interest. On the one hand, measurement of the rheological properties of the reaction mass in the course of the process constitutes a way of following the latter. On the other hand, the intrinsic characteristics of the rheological properties are of direct technological interest: in the field of the conservation of the fluid state—for the assessment of the possibility and ways of filling the mould or the impregnation of the reinforcing structure; after the formation of an involatile product—for the direct assessment of the mechanical (operational) properties.

It is noteworthy that many methodological procedures and experimental methods used to investigate the rheokinetics of the hardening of RO are related to or are analogous to the procedures and methods employed in the technology of processes such as the "monomeric" or "cast" moulding, where the final product is a linear polymer below the melting point and not a cross-linked polymer.[6-9] This enhances the generality of the rheokinetic problem and at the same time poses a new question concerning the role of deformation in chemical processes leading to the formation of the final product. Furthermore, the role of the non-isothermal conditions in hardening processes,[10-12] which is due to the significant exothermicity of the chemical reactions, leading to hardening, as well as the dissipative heat evolution during the flow of highly viscous liquids and the heating from an external source, must be emphasised. The non-isothermal nature of the process itself leads to a series of new phenomena which are of general importance for its kinetics and mechanics.[10,11]

II. CHANGES IN THE RELAXATION STATES DURING HARDENING

The rheokinetic transformations during the hardening of RO are associated not only with a change in the molecular structure of RO (with increase in the chain length and/or the degree of branching) but also (and possibly primarily) with relaxational transitions occurring even under isothermal conditions at the moulding temperature T_m as a consequence of the shift of the glass point T_g of the polymer formed. This fundamental approach was formulated more than ten

years ago and has been developed in numerous investigations.[13-20] Its essential feature is illustrated in Fig. 1, which presents the relaxation processes as a function of T_m in a schematic form. Several main situations are possible. Firstly, the temperature T_m may be higher than the glass point of the final product $T_{g,\infty}$ which is thus in a highly elastic state. During the hardening process, the initial liquid loses its fluidity at some instant as a consequence of the formation of a gel (there is a transition from the fluid to the highly elastic state) and the reaction is completed in the gel. Secondly, T_m may be lower than $T_{g,\infty}$ and a gel is then formed initially (i.e. there is a transition from the fluid state to the highly elastic state) and this is followed by the conversion of the gel into a glass as a consequence of the further progress of the reaction involving the formation of cross-links. Thirdly, at still lower values of T_m, the reaction mass can vitrify before the formation of the gel, which results in the cessation of the structure formation process at an extremely early stage. Fourthly and finally, T_m may be below the glass point of the starting material $T_{g,0}$ and the hardening reaction does not then occur at all.

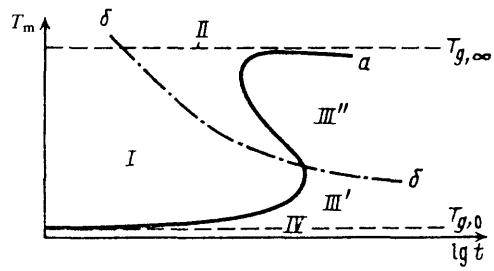

Figure 1. The relaxation states and transitions in the oligomer hardening processes.[18]

The possible situations are clearly seen from the temperature–time diagram (Fig. 1), which has been subdivided into a number of regions by the vitrification lines of the starting material ($T_{g,0}$) and the final product ($T_{g,\infty}$), the line of the gel formed (line *aa*), and the gelation line—the line corresponding to the transition from the fluid to the highly elastic state (line *bb*). Correspondingly I represents the region of the fluid (liquid) state, II the region of the highly elastic state, III′ the vitreous liquid, III″ the vitrified elastomer, and IV the region corresponding to the existence of the vitreous reactive starting material which does not, however, react. The pathway followed by the isothermal reaction is represented by the horizontal line, which intersects lines *aa* and *bb*; at the instant corresponding to this intersection, relaxation transitions take place, which are observed, for example, by the attainment of maxima in the tangent of the mechanical loss angle tan δ.[13]

A rheological method for monitoring the process can be chosen accordingly on the basis of the position of the T_m = const. line (the "reaction pathway"). In region I this is viscometry but, as line *bb* is approached, the viscosity increases without limit and the material loses its fluidity. In all the remaining regions the state of the reaction mass can be inferred from the modulus of elasticity and the tangent of the mechanical loss angle. We may note further that I is the region where the material is "live", i.e. is in a state where it is possible to impart to it the required form; in region II the chemical reaction may continue; in regions III–IV the reaction is significantly arrested possibly long before the attainment of the state of equilibrium. This implies in addition that the properties of the resulting product may depend to a very great extent on the reaction pathway (i.e. on the character of the time variation of the temperature) and that they can be altered by raising the temperature relative to T_m.[21-23]

The diagram presented in Fig. 1 is fairly universal and its configuration is therefore important for various systems capable of hardening and it is also important to establish the exact form of the transitions line. The last problem is evidently associated, primarily, with the description of the macrokinetics of the hardening process and, secondly, with the specification of the character of the dependence of the transition temperatures on the composition (and structure) of the oligomeric products. The first of these problems is of general importance for the problem considered here and the next Section of the review is devoted to it. The second problem was dealt with in a fairly general form by Enns and Gillham[18] and therefore merits further analysis and solution in relation to the principal classes of hardening systems.

III. THE MACROKINETICS OF THE HARDENING PROCESS

1. General Characteristics

A description of the kinetics of the hardening of reactive oligomers is one of the central problems in this field, whose solution makes it possible, firstly, to draw inferences about the chemistry of the process, secondly, to introduce a quantitative parameter in order to compare various materials, and, thirdly, to justify the predictions of the course, productivity, and efficiency of real technological processes. Here there is a possibility of two significantly different approaches: the kinetic and macrokinetic approaches. In the first case the changes in the concentrations of particular reactive groups are inferred by direct physical or spectroscopic methods. This procedure is quite evident and yields clear results, but is by no means always effective from the standpoint of the assessment of the extent and degree of hardening and also the characterisation of the products obtained. This is associated with the fact that the hardening process consists of a set of very many reactions, occurring both simultaneously and consecutively and that the same reactions (reactions of the same chemical type) can lead to the formation of materials with completely different properties, since the topology of the products of isotypical reactions may be fundamentally different.[1,24-26] This method for the estimation of the extent of the hardening reaction is therefore undoubtedly of independent importance, but by no means always leads to an exhaustive solution of the problem.

The macrokinetic method, based on the observation of the time variation of a particular integral parameter reflecting the entire set of the chemical reactions occurring in the hardening of the oligomer, is more widely used and is apparently more effective in practice. Here it is possible to indicate in principle three main methodological approaches. In the first, the concentration of the reactive groups is measured by a chemical or physicochemical method and its time variation is described by a suitable equation regardless of which reactions are undergone by these groups and without specifying in detail the individual stages of the chemical process. In the second method, which may be

called "calorimetric", one measures the time variation of the total heat of reaction and the question which particular possible reaction makes a given contribution to the observed heat change is not discussed. Thus, if the total heat of the hardening reaction is Q and an amount of heat $q(t)$ has been evolved at time t, then the quantity $\beta_c = q(t)/Q$ is adopted as the "calorimetric" degree of conversion β_c.

Such an estimate is very widely used in practice but it has an unambiguous physical significance only when Q does indeed correspond to the overall transformation. This can occur (naturally for a sufficiently long observation) when the final product remains in the highly elastic state. On the other hand, when the reaction mass vitrifies before the completion of the hardening process, then the quantity Q corresponding to the attainment of line *bb* in Fig. 1 is found to depend on the temperature T_m and the quantity β_c, calculated as the ratio $q(t)/Q(T)$, does not characterise the degree of reaction, because different degrees of reaction correspond to the same value of the ratio at different temperatures.[27,28]

The third common method for the estimation of the degree of reaction is based on the measurement of a particular physical characteristic of the substance which depends on the degree of reaction, for example, the viscosity, the modulus of elasticity, hardness, etc. Thus, if the modulus of elasticity of the starting material is G_0, that of the final product (in the highly elastic state) is G_∞, and that of the reaction mass at a certain instant is $G(t)$, then the quantity $\beta_r = [G(t) - G_0]/(G_\infty - G_0)$ may be adopted as the "rheological" extent of reaction β_r. An additional consideration supporting the introduction of this measure of the degree of hardening may be the familiar concept according to which the modulus of elasticity of oligomers capable of being hardened is related to the density of the network of cross-links.[23-25]

It is noteworthy that in the general case one cannot expect β_c and β_r to be identical or to agree with other possible characteristics of the macrokinetics of the hardening process, because these quantities may reflect different reactions of the test substance.

It has been shown that the instant of the attainment of the gel point in no way affects the values of β_c, β_r, as well as other measures of the extent of the hardening reaction employed in the literature. However, this instant (the reaction time corresponding to it will be designated by t^*) is always of independent interest for the physical chemistry and technology of reaction oligomers; t^* also constitutes a macrokinetic measure of the extent of the hardening process and its temperature variation is an important characteristic of the reaction. The value of t^* must therefore be estimated by other procedures, for example, from the instant of the attainment of the maximum in $\tan\delta$ [13,15] or from the instant when the viscosity η reaches a certain arbitrary high level,[29] or when one can assume that $\eta \to \infty$.

The appearance of a residual equilibrium (relaxation) modulus of elasticity or modulus of high elasticity may serve as reliable evidence for the attainment of the gel point, i.e. for the formation of a continuous three-dimensional network.[30] Naturally, it is fairly difficult to determine experimentally whether a non-zero component of the modulus has appeared. The instant when the modulus of elasticity reaches a certain not very high but easily measurable value, for example 10^3 Pa, may be adopted as an experimentally unambiguous (but more arbitrary) criterion of the attainment of t^*.

It is of interest to note that the time t^* determined in this way is correlated[30] (at least in certain cases) with another arbitrary but also unambiguously determined time, namely that when $\tan\delta = 1$ is attained. The latter estimate may be particularly valuable in practice, because it has been established for nine different thermoreactive resins[31] that the times t^* determined by the standardised ASTM method (the resin to be hardened is slowly stirred by hand with a wooden rod and t^* is assumed to correspond to the instant when the rod breaks owing to the high viscosity of the mass) and as the point at which the true (G') and imaginary (G'') components of the modulus of elasticity become equal (i.e. $\tan\delta = 1$) are similar for systems in which t^* varies over a very wide range—from 1 to 1000 min. Bearing in mind the arbitrary nature of the estimate of t^* from the strength of the wooden rod, it becomes evident that the method based on the measurement of the modulus of elasticity is naturally preferable (if one disregards the fact that it requires an expensive measuring technique). The choice of frequency is important for the measurement of the modulus of elasticity, because t^* depends on the frequency. Indeed an increase of the frequency by an order of magnitude corresponds to a shift of the point t^*, at which $G' = G''$, approximately by 1 min along the time axis, which corresponds to a frequency dependence of the relaxation transition point. A frequency of 1.6 Hz ($\omega = 10$ rad s^{-1}), which is approximately equal to the rate of shear used in tests by the ASTM method, is therefore recommended as "standard".[31]

The method of estimating t^* as the time when $\tan\delta = 1$ is very clear and unambiguous; however, generally speaking, it should not be correlated with other methods. Thus in a study of the hardening of unsaturated polyester resins it was found[27] that the point at which $\tan\delta = 1$ coincides with the gel point found by the ASTM method only at low hardening temperatures; with increase of temperature, $\tan\delta = 1$ is reached earlier than the maximum in the loss modulus G'' characterising the instant of the transition.

It is thus evident that, just as one cannot expect a complete correspondence between β_c and β_r, the values of t^* estimated by different methods may not agree owing to the arbitrary nature of the methods employed; only the estimate of t^* from the time when $\eta \to \infty$ is absolute, but the very determination of the attainment of the situation (which can be achieved only asymptotically) also involves greater or smaller errors.

As regards the method used to describe the $\beta(t)$ relation, the essential feature of the macrokinetic approach used to solve this problem is expressed by the equation[4,10]

$$\dot{\beta} = K_0 f(\beta) e^{-U/RT} , \qquad (1)$$

where K_0 is a normalising multiplier, U the activation energy for the hardening process, and $f(\beta)$ a macrokinetic function. The reason for its introduction is that it includes only one variable parameter, namely the degree of reaction β, i.e. in this approach one deliberately ignores the different, possibly very complex, variants of the hardening reaction as a multi-stage process or as a reaction proceeding via several parallel pathways, etc., all this being approximately generalised by the single factor β.

Generally speaking, this approach does not guarantee success and one cannot claim *a priori* that it is applicable in all possible situations. However, the experience gained in describing the hardening processes involving a very large number of oligomers demonstrated the fruitfulness of this approach and the possibility, when the form of the function $f(\beta)$ has been selected appropriately, of describing with its aid all situations encountered in reality. Thus the problem reduces to an appropriate selection of the type of macrokinetic function $f(\beta)$.

Apparently the most general approach to the choice of the function $f(\beta)$ has been proposed by Kamal and Souraur[32,33] and Progelhof and Throne,[34] who formulated a macrokinetic hardening equation [Eqn.(1)] in the isothermal case as follows:

$$\dot{\beta} = (k_1 + k_2\beta^m)(1-\beta)^n \qquad (2)$$

where k_1, k_2, m, and n are empirical constants and k_1 and k_2 can vary with temperature in different ways, while m and n are independent of temperature.

In contrast to many early investigations,[35-38] where an nth order equation was proposed for the description of the macrokinetics, i.e. it was assumed that $f(\beta) = (1-\beta)^n$, Eqn.(2) takes into account explicitly the autoacceleration or autocatalytic effect, expressed by the first multiplier on the right-hand side of Eqn.(2), which is important for hardening reactions.

An undoubted advantage of Eqn.(2) is its general character, while its disadvantage is its extreme generality, since four "adjustable" constants are as a rule too many to achieve an unambiguous macrokinetic characteristic of the hardening process. In most cases it is therefore sufficient to employ simpler relations which are special cases of Eqn.(2).

Thus the macrokinetics of the formation of polyamide-6 are described by an equation of the autocatalytic type but in a much simpler form, which is obtained from Eqn.(2) when $m = n = 1$ on the assumption that the reaction rate constant obeys the Arrhenius relation as a function of temperature:[9,39-42]

$$\dot{\beta} = K_0 e^{-U/RT}(1-\beta)(1+C\beta)\ , \qquad (3)$$

where there are only two "adjustable" parameters, K_0 and C, which vary as a function of the conditions of the synthesis, i.e. the concentrations of the catalyst and the activator, the nature of the active centres, etc., while U is the activation energy for the polymerisation process.

The macrokinetics of the formation of polyamide-12 from dodecalactam are described by a first-order equation without an autocatalytic term, i.e. in this case $C = 0$;[8,9,41] however, this is of course an exceptionally simple and atypical case.

There is no doubt that Eqn.(2) represents the most general case, but in practice it is nevertheless desirable to have fairly simple values of the constants m and n.

2. The Macrokinetics of Structure Formation in the Principal Types of RO

We shall now consider the principal results of the application of the macrokinetic method to the description of the hardening of the RO described in the literature. The most important and most frequently investigated case, to which the greatest number of communications have been devoted, is the hardening of epoxide resins. It has been shown that Eqn.(2), where β has been most often determined from the results of calorimetric measurements, is entirely suitable for this case with the constants $m = n = 1$.[32,33,43,44] This conclusion terminates a fairly prolonged controversy concerning the character of the macrokinetic equation for the description of the hardening of epoxide resins, because earlier various publications proposed equations for $f(\beta)$ of zero,[45] first,[46] and fractional[47] orders in the degree of reaction. The conclusion that the hardening reactions of epoxide resins proceed with autoacceleration, reached by Kamal,[33] can also be found in Rozenberg's paper[48] (on the basis of data obtained calorimetrically, i.e. β_c), and was later confirmed also by the rheological method,[49] i.e. on the basis of β_r. In the last study β was determined for the hardening of the diglycidyl ether of bisphenol-A with dicyanogendiamine and it was established that the constant k_2 in Eqn.(2), characterising the autoaccelerating effect of the reaction, is fairly high, but the autoacceleration effect degenerates with increase in the concentration of the hardening agent.

The question of the temperature variation of the rate or duration of the structure formation reaction is important (in both practical and theoretical respects). Here one must emphasise that the effective activation energy U can be determined by various methods, which generally speaking can yield different results depending on the choice of conditions in comparing the values of the given parameter under non-isothermal conditions. Thus U found from the gelation time, i.e. from the gel point t^*, may not agree with the value determined from the temperature variation of the maximum rate of change of β or from the time coresponding to the attainment of a specific level of the values of β, etc. Whether or not the values of U found by different methods agree depends on the form of the macrokinetic equation for $\dot{\beta}$ and on the presence or absence of an influence by temperature on the constants which it includes.

The discrepancy between the values of U found from different characteristic points has been demonstrated very clearly in a study[50] where it was found that $U = 55$ kJ mol^{-1} when it is calculated from the point corresponding to the onset of gel formation, $U = 66$ kJ mol^{-1} when found from the most rapid increase of the modulus of elasticity (the rigidity of the material), $U = 83$ kJ mol^{-1} when found from the instant corresponding to the completion of the rapid increase of the modulus, and, finally, $U = 103$ kJ mol^{-1} when found from the time of attainment of the final value of the modulus. The observed monotonic increase of U as one moves from the beginning to the end of the reaction is fairly striking, because it apparently shows that the two constants which determine the macrokinetics of the structure formation process nevertheless vary with temperature in different ways, so that a single value of U does not exist. In this respect an unusual simple exception is provided by the situation described by Malkin et al.,[49] who found that the autoacceleration constant is independent of temperature and the effective activation energy (70 kJ mol^{-1}), determined from $\dot{\beta}$ (or from the rate constant $K = K_0 e^{-U/RT}$) proved to be identical with the values calculated from the temperature variation of $1/t^*$ and from calorimetric data published previously.[46]

However, one should note that in Eyerer's study[51] the activation energy calculated from spectroscopic data for different stages of the reaction with bisphenol-A and dicyanogendiamine was also found to be the same in all cases but its value was 84 kJ mol^{-1}. The significantly smaller value $U = 51$ kJ mol^{-1}, obtained[19] for the reaction of a mixture of diglycidyl ethers with 2,4-tolylene-1,1'-bis-3,3-dimethylurea contrasts significantly with the high values of U quoted above.

Naturally the specific value of U depends on the detailed composition of the reaction mass, because the rate-limiting reaction may be various. Thus the effective activation energy for an epoxyorganoelemental oligomer, hardened with oligobutoxytitanophosphoroxan, found from the temperature variation of $1/t^*$, varied in the range 47–60 kJ mol^{-1} as a function of the content of the hardening agent.[52]

Somewhat more detailed results of a macrokinetic study of the structure formation process in epoxide resins (without specification or the hardening composition) have been given in a communication[53] based on certain earlier results of calorimetric studies.[54-56] The authors[53] observed, firstly, that the curves obtained by the method of differential

scanning calorimetry show two "humps", which correspond to the existence of two different main reactions and, secondly, that the $\beta(t)$ relation is described in different ranges of β by different macrokinetic equations; a first-order equation, where $U = 56.6$ kJ mol^{-1}, proved to be fairly suitable for $\beta > 0.3$. For low values of β, the rate of reaction is described by an extremely complex equation incorporating two constants which vary with temperature in different ways, so that there is no single activation energy.

Apparently if one follows the "averaging" procedure, then $U \cong 84$ kJ mol^{-1}, which should be adopted[46,57,58] as the most reliable (most frequently quoted in the literature) value of U for the reactions of epoxide resins; however, it has been pointed out[57] that cases are possible where the temperature variation of the rate of reaction (or t^*) is not described by the Arrhenius relation at all and in another communication[58] even lower values of U have been quoted. (Other values of U and different methods for describing the temperature variation of the hardening of epoxide resins were mentioned above.)

In conclusion of the discussion of the macrokinetics of the hardening of epoxide oligomers, we shall note also certain facts associated with this reaction. Firstly, one should approach the estimation of β_c with caution, since account must be taken of the very considerable (almost by a factor of two) variation of the specific heat and thermal diffusivity in the hardening process.[44] Secondly, the extent of reaction at the gel point β^* varies very appreciably as a function of composition (functionality) of the reaction mass, but as a rule deviates significantly from theoretical estimates. Thus $\beta^* = 0.3-0.47$ for tetrafunctional compounds (instead of the theoretical value of 0.58), which is associated in the general case with failure to take into account the role of secondary reactions.[57] Values of β^*, varying to a very large extent as a function of the recipe for the hardening of the composition, have been published.[59] Naturally, one may not expect agreement between the values of β^* and the instant of the appearance of the gel fraction in the reaction system.[52] In the general case this is apparently associated with the heterogeneity of the network formed.[50,60]

In connection with the development of the "oligomer" technology, numerous studies on the formation of polyurethanes have been carried out. The macrokinetics of this process have been frequently described by a power relation,[61,62] where $n = 1.5$, which was dictated primarily by the convenience of the solution of hydrodynamic problems involving the use of this equation,[62-64] although the authors who proposed it[61] noted themselves that it yields an insufficiently accurate approximation to the real picture of the phenomenon. The kinetics of the formation of polyurethanes have been described[65] by a second-order equation on the basis of the results of measurements by differential scanning calorimetry (DSC). A more complex two-term equation, reflecting both the forward second-order reaction and the reverse first-order reaction, has also been proposed.[66]

In reality the reaction under discussion is fairly complex and a second-order equation, which seemingly should be sufficiently effective at least when a bifunctional hardening agent is employed, is inapplicable to the entire polymerisation process, although it can describe successfully shorter or longer parts of the process.[67] As in the previous case, the most complete and exact description of the $\beta(t)$ relation for polyurethanes can be achieved when a macrokinetic equation of type (2) is employed. However, a significantly new aspect of this equation has been discovered precisely in relation to polyurethanes, namely it was found[68] that the constant $C < 0$ in Eqn. (3), which is the main special case of Eqn. (2). This means that the hardening reaction does not in principle go to completion: when $\beta = C^{-1}$, the rate of the process falls to zero, i.e. the reaction stops at this value of β and this happens under both isothermal and adiabatic polymerisation conditions.

The third main system to which numerous studies on the macrokinetics of the hardening process have been devoted consists of unsaturated polyester resins. In essence, an equation of type (3) has in fact been formulated precisely for such substances as well as epoxide resins,[32,44,69,70] although a simpler power equation had been used in the very earliest publications.[71] Later studies confirmed the validity of the macrokinetic equation (3).[27,28,72-76]

It is of interest to note the following results of these studies. Firstly, the sum of the exponents $m + n = 2$, which reduces the number of "adjustable" constants. Secondly, m and n are almost independent of temperature (the variation of m and n with temperature has been indicated only by Han and Lem[27]). Thirdly, whereas both k_1 and k_2 depend on temperature very markedly, their ratio, characterising the autoacceleration effect in the hardening process, is almost insensitive to changes in temperature. The effective activation energy calculated by many investigators from k_2 is in the range 76 ± 3 kJ mol^{-1}; Han and Lem also quote a value of U calculated from k_2 which is significantly higher (approximately 103 kJ mol^{-1}) than that found from the temperature variation of k_1. Only Yap and Williams[77] quote an appreciably lower value $U \cong 40$ kJ mol^{-1}, found from the temperature variation of the dynamic modulus of elasticity measured at a fixed frequency.

The values of m and n found by different workers are quoted below:

m	0.25	0.33	0.45	0.49
n	1.75	1.67	1.55	1.51
References	[32]	[69]	[70]	[27]

It is of particular interest to note that the critical gel point β^*, defined as the instant when $\eta \to \infty$, depends to a large extent on temperature.[27,28] Apparently this is associated with the influence of temperature on the degree of heterogeneity of the polymer structure formed.

There have been few studies devoted to the macrokinetics of the hardening of systems other than the three enumerated above. These are primarily studies concerning the hardening of the methylphenylsiloxane oligomer[78,79] and other low-molecular-weight organosilicon rubbers.[80] Although limited regions of variation of β can be described by nth order equations (in particular those where $n = 2$),[78] nevertheless extended ranges of values of β necessitate the employment of a macrokinetic equation of type (2) or (3). Incidentally, in certain cases, similarly to what has been observed for polyurethanes, there is a possibility of a situation where $C < 0$.[80]

It is also possible to find other examples of studies on the kinetics of structure formation in various products (not necessarily hardening): in certain instances this can be cyclisation,[81] the copolymerisation of organsiloxane oligomers,[82] various intrachain transformations,[15,83,84] etc. However, the experimental data quoted in these and other reports have not been subjected to a realistic quantitative macrokinetic analysis, in view of which their consideration is somewhat outside the framework of the present review.

Problems associated with the non-isothermal nature of volumetric data occupy an important place in the consideration of the macrokinetics of hardening processes.[10-12]

There is a possibility of three sources of non-isothermal conditions: heat exchange with the ambient medium, the exothermicity of the reaction, and the dissipation of the work due to external friction. When non-isothermal macrokinetics are considered, the cause of the local change in temperature is insignificant, but the external source of heat usually plays a smaller role than the internal sources. The factor associated with dissipative heat evolutions will be considered below in the section devoted to the rheology of the RO. Here we shall concentrate attention on the exothermic effects, particularly since in many cases of practical importance hardening can occur under virtually adiabatic conditions and the temperature rise due to the exothermic nature of the reaction can exceed 100 °C.[85]

It is therefore extremely important to have at one's disposal a method for calculations on hardening under non-isothermal conditions. It is based on the integration of Eqn.(1) taking into account the familiar $T(t)$ relation or the relation specified by the course of the process itself; such a relation is simply formulated in an adiabatic regime:[10,11]

$$T(t) = T_0 + \frac{Q}{c\rho}\beta \quad ,$$

where Q is the total heat of reaction, c the specific heat, ρ the density, and T_0 the initial temperature. In the general case the factor $c\rho$ can depend on T, which requires an independent consideration. When this expression is substituted in Eqn.(1), we obtain an equation containing only one unknown function $\beta(t)$, which can be found by numerical methods. Naturally, the function $T(t)$ is then also found without difficulty. In essence, a completely analogous approach is applicable when the temperature variation of $\dot{\beta}$ is described by a non-exponential equation, for example the familiar Williams–Lundell–Ferry equation.[86] Such a generalised approach is applicable also in the calculation of the variation of viscosity under non-isothermal conditions.[59,87]

The calculation of $\beta(t)$ and $T(t)$ not in an adiabatic regime but under conditions involving partial removal of the heat of reaction to the ambient medium is more complex but quite feasible at the present level of development of computer techniques.[8]

The change in the temperature of the system in the hardening of RO plays such an important role that on this basis it is possible to propose a method for the monitoring and regulation of the technological process by measuring the temperature at separate points in the material being hardened.[88]

Various aspects of the problem of non-isothermal polymerisation (and hardening) have been considered in detail in reviews.[10–12] Here we should like to mention only one phenomenon associated with non-isothermal conditions—the frontal propagation of the reaction as a consequence of the exothermic nature of the process occurring during its "ignition" in a certain local region,[12,89,90] which is one of the most effective methods of carrying out the hardening process. This phenomenon is of general importance and may arise in reactions of different types—radical polymerisation,[91] polymerisation in suspension,[92] etc. It has been shown recently[93,94] that frontal polymerisation can also occur in a combined process, namely when the heat evolution due to the crystallisation of the product formed is superimposed on the exothermic effect of the polymerisation reaction. Although it is still obscure whether such a "running wave" can arise in the hardening process, there is no doubt about its possibility for the related "chemical moulding" process in the activated ionic polymerisation of lactams.

In concluding this section we may note that the macrokinetics of the hardening process in both isothermal and non-isothermal cases can be deduced fairly simply if the reaction takes place in the kinetic region. On passing to the diffusion-controlled region, the situation becomes fundamentally more complex until even the adiabatic temperature rise, characterising the extent of reaction, begins to depend on the rate of stirring characterised by the Reynolds number.[95] Nevertheless, from the standpoint of the mathematical modelling of the RO hardening process as a whole, which is central to the aim of the present review, the situation is simplified by the fact that, so long as the reaction takes place in the supply channels where the flow (and mixing) take place, the viscosity of the medium is low, the material is homogeneous, and one can assume that the initial stages of the hardening process take place in the kinetic region. After the mould in which the RO hardening process proper is completed has been filled, there is no flow at all, the reaction takes place in a non-deformable material, and its macrokinetics therefore reflect the situation which, although possibly in fact complex, is similar for comparable conditions, i.e. for various recipes and different geometrical dimensions of the article.

IV. THE RHEOLOGY (RHEOKINETICS) OF THE HARDENING PROCESS

Two rheological methods are most widely used to follow the kinetics of structure formation in oligomers: from the change in viscosity η and from the change in the modulus of elasticity G, the latter being susceptible to measurement also in the dynamic regime of periodic oscillations.[4,5] The general character of the variation of η and G with time t is illustrated in Fig. 2, the scheme referring to the case where $t > t^*$ and the system undergoing hardening is in a highly elastic (or gel-like) state, so that the hardening reaction can go to completion. It is striking that the modulus of elasticity begins to increase before the time t^* has been reached. This phenomenon is observed when the initial oligomers have a chain sufficiently long to manifest its flexibility or when the formation of cross links is accompanied by an increase in chain length (by a continued increase) when the reactive end groups interact. In such cases the appearance of the condition $G \neq 0$ is due to the formation of physical entanglements, contributing to the network structure, which is formed as a whole as a consequence of the existence of nodes of not only chemical but also physical nature.[96] It is likewise of interest to note that the attainment of t^* is not as a rule reflected in the character of the increase of the modulus, whereas viscosity rises very sharply as this point is approached: at $t \to t^*$ the material loses its fluidity ($\eta \to \infty$).

The character of the variation of the modulus of elasticity during the hardening process, largely discussed in the previous Section, where the quantity β_r, calculated from the relative change in the modulus of elasticity during the hardening process, was proposed as one of the possible parameters for the estimation of the extent of reaction. This in essence exhausts the problem of the macrokinetic description of the hardening process in terms of the change in the modulus of elasticity, particularly if we consider in addition that the measurement of the modulus G belongs to the same series of physical methods for monitoring the RO hardening process as the methods for following the hardening kinetics: by a dielectric procedure from the change in the dielectric constant and in the tangent of the dielectric loss angle (fairly numerous communications have

been published on this topic; among them, mention may be made of those of Badalov et al.[97] and Siemon et al.[98]), from the change in the electrical conductivity of the composition,[99] from the spin–spin relaxation time measured by the pulsed NMR method,[100] from the change in the refractive index,[101] etc.

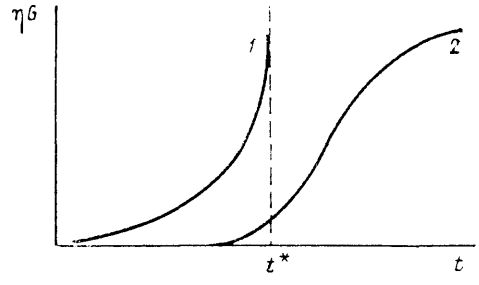

Figure 2. Character of the variation of the viscosity (curve *1*) and the modulus of elasticity (curve *2*) with time in the oligomer hardening process.

However, viscometric measurements in the region where $t < t^*$ are of independent importance. Firstly, in this region all the methods based on the measurement of the density of the network of cross links are unsuitable (because at this stage of the hardening process there is as yet no network); secondly, the measurement of the $\eta(t)$ relation is central for the technological monitoring of the "liveness" and quality of the RO and compositions based on them; thirdly, the quantitative estimate of the $\eta(\beta)$ relation constitutes the basis for the solution of all the hydrodynamic problems associated with flow in the casting channels, with the filling of the mould, etc.; fourthly, and finally, measured viscosities can be compared directly with the molecular characteristics of the test substance, particularly when one is considering not structure formation but an increase in chain length in the interaction of the end groups or in polymer-analogue transformations within the chain.

At the present time equations of two types for the description of the $\eta(t)$ relation in the hardening of RO are being discussed. In equations of the first type it is assumed explicitly that, when $t \to t^*$, the viscosity increases without limit. In equations of the second type a sharp, usually exponential, increase of viscosity is also postulated, but the equation itself formally does not have a singularity.

Among the equations of the first type, power expressions which follow from scaling ideas are of greatest interest:[102–105]

$$\eta \propto (\beta^* - \beta)^{-s} \quad . \tag{4}$$

Equations of this type are applicable over a very narrow range of β near β^* when $(\beta^* - \beta)/\beta^* \ll 1$; since it can be assumed that $\beta \propto t$ over such a narrow range of values of β, instead of Eqn.(4) one formulates a relation which is analogous in structure:

$$\eta \propto (t^* - t)^{-s} \quad , \tag{5}$$

where s is a constant, which, according to the available measurements[105] for two systems of different chemical types, amounts to 0.78 ± 0.05 and this result agrees with the theoretical estimate obtained by Monte Carlo methods.[105]

As regards the question of the relation between the viscous properties of the hardening RO and its molecular characteristics, this has been studied most systematically and solved for polyurethanes, probably because hitherto this has been virtually the only system to which the "oligomeric" moulding method, requiring serious quantitative calculations, has been applied on an industrial scale.

According to the available data,[62,106,107] the dependence of the viscosity η on the weight-average molecular weight $\bar{M}_w$ is expressed by the formula

$$\eta = A\bar{M}_w^a \exp\left(\frac{E}{RT}\right) \quad , \tag{6}$$

where A, a and E are constants. In this approach it is most important that $\bar{M}_w$ should be unambiguously related to the degree of reaction and one obtains $\bar{M}_w \to \infty$ when $\beta \to \beta^*$ and hence $\eta \to \infty$, i.e., firstly, in Eqn.(6) the existence of the gel point is expressed explicitly and, secondly, it is possible to establish an unambiguous function $\eta(\beta, T)$. The latter has been achieved by Castro and co-workers,[108,109] who showed that the entire set of experimental data for the $\eta(\beta, T)$ relation can be described by the generalised formula[108,109]

$$\frac{\eta(\beta, T)}{\eta_0(T)} = \left(\frac{\beta^*}{\beta^* - \beta}\right)^{A + B\beta} \quad , \tag{7}$$

where η_0 is the initial viscosity of the system. Here the influence of temperature on the viscosity has been expressed by the relation $\eta_0(T)$, provided of course that one disregards the influence of temperature on the hardening kinetics. It is also of interest to note that in all the instances investigated the constants A and B assumed the "universal" values $A = 3.5$ and $B = -2.0$.

The existence of such a generalised relation $\eta(\beta, T)$ is specially remarkable, since the reaction under discussion was not carried out under homogeneous conditions but was accompanied by phase separation;[108,110] nevertheless, it has been possible to find a general law governing the variation of viscosity which is valid during the period from the start of the reaction directly until the attainment of the gel point, i.e. for a change of viscosity within a range corresponding to five decadic orders of magnitude.[106]

It is at present difficult to say whether this approach can be extended to other RO. In a qualitative form the answer should probably be yes, but the search for optimum specific quantitative relations still remains an independent and laborious problem. In this respect one must emphasise that there is a possibility of specific problems for each system. For example, in the hardening of polyesters not only an increase of β^* with increasing temperature accompanied by the corresponding displacement of the $\eta(\beta)$ relation towards higher values of β but also the possibility of a flow of the polymer, albeit with a lower viscosity, under conditions where $\beta > \beta^*$, associated with the formation of a highly heterogeneous suspension, has been observed.[27] In the hardening of epoxide resins at different temperatures it was established[58] that the $\eta(t)$ relations can be superimposed by a vertical shift of the plot by an amount a_η and a horizontal shift by an amount a_t. The effective activation energy for viscous flow can be found from the temperature variation of a_η and the corresponding activation energy for the cross-linking process can be found from the corresponding temperature variation of a_t.

Equations of the second type, proposed for the description of the variation of viscosity in the hardening of RO, do not take into account explicitly the existence of the gel point, which is clearly seen in the most widely used of the

equations:[32,33]

$$\eta=\eta_0 \exp(kt) \quad , \tag{8}$$

where η_0 is the initial temperature-dependent viscosity and k a constant characterising the influence of the rate of the chemical reaction on the increase of viscosity, which depends in its turn on temperature, so that one can write

$$\eta_0=\eta_\infty \exp(E/RT) \quad , \tag{9}$$

$$k=k_\infty \exp(U/RT) \quad . \tag{10}$$

Evidently the influence of temperature on viscosity is manifested to a greater extent via k than via η_0, because in the former case the exponential function occurs twice. It also follows from Eqn.(8) that $\eta \to \infty$ only when $t \to \infty$, so that it would seem that the gel point does not exist. Naturally, this is only a formal conclusion, since evidently it is almost always possible to adopt as t^* the time corresponding to the attainment of a certain constant level of viscosity; however, in the solution of applied problems Eqn.(8) may prove to be more convenient than the formulae examined previously, which are formally more rigorous. The equation with argument β can be formulated analogously:

$$\eta=\eta_0 \exp(k'\beta) \quad , \tag{11}$$

$$k' = k'_\infty \exp(E'/RT) \quad . \tag{12}$$

The use of Eqns.(8)–(12) makes it possible to extend the $\eta(t)$ relation readily to the case of hardening under non-isothermal conditions, which has been analysed in detail in a review,[5] so that this question will not be considered here.

Equations of type (11) have indeed been used successfully to describe real hardening systems. Thus Eqn.(11) describes with satisfactory accuracy[53] the $\eta(\beta)$ relation for the hardening of epoxide resins with viscosity varying over a range of three decadic orders of magnitude; here it was found that $k' = 14.1 \pm 1.2$. On the other hand, the effective activation energy E reflecting the temperature variation of viscosity proved to be 90.8 kJ mol^{-1}, which exceeded appreciably the activation energies found from β_c (these were discussed above). This finding is the evident consequence of the fact that E "incorporates" the activation energy for the chemical reaction and viscous flow and these quantities are not additive.[4,111,112]

In view of the practical importance of formulae of the exponential type, it is of interest to establish correlations between their constants and the characteristics of the compositions based on the RO. This is an extremely promising procedure for the quantitative estimation of the quality of the initial materials to be hardened. Numerous instances referring to this approach have been described.[59] In essence, a method for the estimation of the efficiency of catalysts of the formation of polyurethanes in a chain propagation reaction has been proposed on the basis of an analogous idea but without a mathematical treatment.[113]

The use of rheological methods for the investigation of the macrokinetics of the hardening of RO gives rise to certain questions concerning the role of the rate of deformation, namely (1) does the rate of shear $\dot{\gamma}$, at which measurements are made, influence the character of the $\eta(t)$ relation, i.e. the kinetics of the process; (2) what is the form of the rheological equation, i.e. of the dependence of the effective viscosity on the rate of shear $\eta(\dot{\gamma})$ for different stages in the hardening of RO. Apparently there is no general answer to these questions and the answers can be different depending on the nature of the reaction mass.

As regards the role of the rate of shear $\dot{\gamma}$, it has been found that $\dot{\gamma}$ does not usually influence the rate of increase of viscosity. At any rate special studies of this question, referring to the formation of polyurethanes, have shown[108] that, even under phase separation conditions, neither a change in $\dot{\gamma}$ nor a transition from continuous to periodic (only at the instant of the measurement of viscosity) deformation influence the observed character of the increase of viscosity $\eta(t)$. Apparently this situation corresponds to polymerisation under homogeneous conditions, while on passing to the heterogeneous region one should expect deformation to influence the rate of hardening. Thus it has been demonstrated theoretically[114] that in diffusion-controlled reactions an increase of mechanical stresses entails an increase of the rate of the chemical reaction. However, in practice, at least in one instance which has been investigated,[115] exactly the opposite picture has been observed: under phase separation conditions (where the polymer formed was insoluble in the reaction medium), an increase in the rate of deformation led to a significant retardation of the reaction.

However, one should note that the amount of experimental data concerning this problem is very small and the available information is not unambiguous. Thus the data quoted in certain communications[116,117] about the influence of deformation on the rate of radical polymerisation are hardly reliable, since, in the deformation regimes employed in the relevant investigations, dissipative heat evolutions apparently occurred to an extent sufficient to cause the change in rate described above as a result of the deviation from isothermal polymerisation conditions (for a description of the role of dissipative heating, see below).[118]

On the other hand, in general the kinetic role of deformation in RO polymerisation and hardening processes has been clearly studied inadequately: neither the scale nor the limits of the manifestation of the influence of deformation on these processes are known at present.

The influence of the periodic shear deformation on the rate of hardening of RO belongs to the same series of phenomena. This effect was first described a fairly long time ago[119] and it was emphasised that periodic deformation influences not only the kinetics of the hardening process but also the properties of the final products. Subsequent publications[120–122] confirmed these observations; however, here too the question of the quantitative description and limits of this phenomenon remains on the whole open.

An unusual instance of the influence of deformation on the RO hardening kinetics is the situation where intense deformation leads to significant heat evolution, which increases in its turn the temperature of the reaction mass and hence appreciably accelerates the hardening reaction. Observations of this kind have been described in two communications[123,124] and subsequently a complete quantitative theory was developed. It explained this effect, agreed with experiment, and virtually ruled out the need for the consideration of deformation as a direct kinetic factor and it related the role of deformation solely to the non-isothermal conditions in the hardening process caused by it.[125–128] This effect can accelerate the hardening of RO by a factor of many tens but only by virtue of the internal non-isothermicity of the process.

Yet another question related to this range of problems is that of the character of the $\eta(\dot{\gamma})$ relation for RO. In the initial stages of the hardening process reactive oligomers are as a rule Newtonian liquids[109,129] which show no elasticity, although anomalous cases are possible.[130] On the whole, in terms of their rheological properties, RO do not differ from any other polymeric materials[131] and the questions associated with the specific features of the behaviour of filled compositions based on the RO have already been discussed.[5] In the solution of applied

problems associated with the chemical moulding of articles from RO, the flowing liquid is usually seen to be Newtonian but with a viscosity which depends on time or on the degree of reaction;[62,63,129,132] sometimes the so-called power law is employed[64] (similarly to what is done in almost all cases where theoretical problems associated with the flow of thermoplastics are considered[133]). The most complete rheological equation of state of this kind includes terms taking into account the existence of a flow region with a constant (most Newtonian) viscosity and also the transition to the flow region (at sufficiently high rates of shear) described by a power law,[64] the effect of the anomalously viscous flow being determined by the dimensionless product $\lambda\dot{\gamma}$, where the relaxation time λ itself depends on the degree of reaction. The onset of this effect shifts towards lower rates of shear the higher the value of λ, i.e. the greater the extent of the hardening process. Next, for filled compositions based on RO, it is necessary to take into account the existence of the yield point,[134] which incidentally has to be done also for any other filled polymer melts (this question has been discussed in detail in an earlier review[5] and for this reason there is no need to dwell on it here).

Although in the absolute majority of instances where the rheology of RO is the subject under discussion their viscous properties are considered, in reality the question should be understood in a broader sense and other characteristics of such media should also be considered. In the first place mention should be made of their elasticity which is characterised by the appearance of normal stresses σ_W.[131] In an earlier communication[135] it was already stated that the elasticity of the material varies in the region of structure formation to a much greater extent than its viscosity. Few measurements have been made of the changes in the elasticity of RO in the hardening process,[27,28] but they all demonstrate both the role of the normal stresses and the methodological difficulties associated with the measurements of σ_W and the treatment of the results of the measurements: during the hardening process, the volume of the RO diminishes, which looks like the manifestation of negative σ_W, although in reality it is not associated with such stresses, which appear in the shear flow of viscoelastic liquids and are of intrinsic interest from the standpoint of the rheology of polymers and the rheokinetics of structure formation in RO.

V. THE FLOW OF REACTIVE OLIGOMERS

The development of the technology of chemical "reactive" moulding aroused interest in a new class of hydrodynamic problems—the flow of liquids whose rheological properties vary with time. The closest analogue of these problems is provided by problems of non-isothermal flow, where viscosity varies with temperature. In the case of RO non-isothermal conditions constitute only one of the aspects of a more complex general problem of flow with a variable viscosity and it is not even the most important aspect. In essence one is dealing with classical hydrodynamic problems in a new formulation.

Within the framework of the present review, it would be inappropriate to consider the mathematical aspect of the problem but it is useful to deal with fundamental starting points. The general formulation of problems concerning the flow of liquids with a variable viscosity has been described in a number of communications,[62–64,66,129,132,136–140] in which the underlying ideas were in essence identical. They involve the introduction into the equilibrium equation for the variation of viscosity either with time or with the degree of reaction; in the latter case it is necessary to consider in addition the kinetic equation for the extent of reaction. The non-isothermal process conditions, caused not only by heat exchange with the walls but also by the dissipative heat evolutions and the exothermic heat of the hardening reaction, do not introduce any fundamental complications into the solution of the problem,[132] although the size of necessary calculations increases. In all cases it is naturally necessary to employ a fairly powerful computer technique in order to obtain quantitative results. The choice of the rheological equation of state does not play a significant role either. However, the formulation of dynamic boundary conditions on the walls of the channel is of fundamental importance. The usual adhesion hypothesis is by no means satisfactory in all cases. The point is that for hardening compositions a time is always attained where $\eta \to \infty$, which corresponds to the formation of a stationary layer sticking to the walls of the channel, which grows with time until the entire channel is "grown over" by a mass incapable of flowing, which in principle rules out the possibility of a steady flow. To ensure the possibility of a steady flow, it is therefore necessary to adopt the hypothesis of slip near the wall.[64,134]

A rigorous formulation of problems concerning the flow in channels of liquids with varying rheological properties, in flows both with and without a head pressure, makes it possible to determine all the significant hydrodynamic characteristics—such as the distribution of velocities, degrees of reaction, and temperatures along the cross-section and length of the channel, as well as the length corresponding to complete reaction. The latter concept does not occur in normal hydrodynamics, but in this instance it is significant, because it characterises the length of the channel necessary for the attainment of a specified degree of reaction β even at the most unfavourable point (for hardening RO, it must be evidently smaller than β^*). The concrete results of calculations associated with such problems are extremely non-trivial and are frequently unexpected; they demonstrate the existence of extremely unusual characteristics of the flow, but their consideration constitutes a separate task and here it is useful to limit the description to initial problems in the formulation and not to undertake a hydrodynamic analysis.

However, whereas problems concerning flow in filled channels are fairly clear in their formulation, those associated with flow in an incompletely filled channel or with the flow of a hardening liquid having a free surface at the front of the flow are not quite so self-evident. Clearly, for the technology of chemical moulding, this problem is no less important than that of the steady flow through fully filled channels, which necessitated the analysis of such problems.

From numerous direct observations, it has long been known that in the region of the front of the flow there exists the so-called "fountain" effect,[63,66,141–143], which consists in the spreading of the liquid from the axial zone to the walls and this leads to a significant equalisation of the residence times of various particles of the liquid in the channel and hence to a considerable change of the entire hydrodynamic arrangement compared with a one-dimensional flow. Thus the flow near the front becomes two-dimensional in contrast to the one-dimensional flow in a filled channel. A rigorous formulation of this problem is very complex and virtually all the investigators dealing with it have pointed out that there is no need for such a rigorous approach, because it is sufficient to adopt an approximate empirical model of the flow of liquid from the centre to the wall based on experimental data[66] and the specification of the flow pattern in the front in greater detail does not introduce

fundamental changes into the final picture. Since there is no doubt that the fountain effect exerts a significant influence on the entire situation in the filled channel (or mould), including the distribution of residence times, degrees of reaction, and molecular and rheological characteristics of the test substance, the choice of an adequate model of this phenomenon remains an extremely important problem in the theory of chemical moulding.

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The initiation and development of the modern technology of the production of polymer articles by chemical moulding have generated a whole series of new problems. The chemical problems associated with the requirements which must be met by the properties of the resulting material have been supplemented by physicochemical problems associated with the necessity to ensure specified hardening kinetics and also mechanical problems, since the rheological characteristics of the products and the characteristics of the flow of the moulded compositions have a decisive influence not only on the properties of the final product but sometimes even the very feasibility of the technological process.

Overall, all these factors make it possible to construct a mathematical model of the hardening of RO and compositions based on them, which enables us to achieve the most important aim (on passing to large-scale technology): to control the process in order to ensure the required quality of the material in combination with the optimisation of the techno-economic process parameters. The transition from general characteristics, which in many respects have already been elucidated, to concrete quantitative results, which can be used in practice requires nevertheless very careful laboratory studies for an adequate quantitative description of the rheology of RO and the macrokinetics of the hardening process in relation to specific materials. The industrial realisation of the results of such research ensures the development of a stable and effective technological reaction-moulding process.

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Three-membered Metallocycles

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The results of structural and theoretical studies on cluster compounds with a framework in the form of a triangle made up of metal atoms are examined, a systematic account is given of the types of three-membered metallocycles in which the number of electrons is different from the "magic" number, and the causes of their stability are analysed. The influence of the ligand shell and of the formation of multiple bonds on the stability of three-membered metallocycles is demonstrated.
The bibliography includes 169 references.

CONTENTS

I.	Introduction	305
II.	Three-membered metallocycles containing the "magic" number of valence electrons	307
III.	Triangular clusters with an excess of valence electrons	311
IV.	Stable three-membered metallocycles with a deficiency of valence electrons	313
V.	The electronic structure of three-membered metallocycles	316

I. INTRODUCTION

The chemistry of cluster compounds, a field undergoing vigorous development at the present time,[1] is at the junction between a number of other fields of science: inorganic chemistry, organoelemental chemistry, catalysis, biochemistry, colloidal chemistry, the physics of ultradisperse systems, the physics of surfaces, and electronic materials science†.

†In the USSR two All-Union Discussion Seminars were held on the chemistry and physics of cluster compounds (1979 and 1981) as well as the Ist All-Union Conference on the chemistry of clusters together with the Ist All-Union Seminar on "clusters in catalysis" (1983). The proceedings of the seminar and the conference have been published in special issues of the journals Izv.Sirbir.Akad.Nauk SSSR, Ser. Khim. (Bulletin of the Siberian Division of the USSR Academy of Sciences, Chemistry Series), 1982, Issue 4, No.9, and Koord.Khim. (Coordination Chemistry), 1984, **10**, No.5.

The term cluster compounds is given to those metal compounds whose molecules contain a framework of metal atoms at distances permitting a direct metal–metal interaction, surrounded by a framework of ligands;[2] the characteristics of the electronic structure of two-centre metal–metal bonds of different multiplicity have been investigated in detail in relation to a series of dinuclear metal complexes[3] (see also other communications[4-9]). Cluster compounds are divided into small (N = 3–12)#,[10-13] medium (N = 13–40),[14-15] large (N = 41–100),[16] and ultralarge or "giant" (N > 100). The framework in cluster molecules can consist of metal chains of different lengths and with different degrees of branching,[17-19] metallocycles,[20] metalloskeletons,[21] metallopolyhedra, as well as combinations of the above structural elements. Cluster

#Here and henceforth N represents the nuclearity of the cluster, i.e. the number of metal atoms constituting the framework of the cluster compound.

compounds are characteristic of transition metals,[22] lanthanides and actinides,[23] and the majority of non-transition metals.[24,25] Heterometallic cluster compounds containing two,[27-30] three,[31] and more different kinds of metal atoms in the molecular skeleton are being vigorously investigated.[26] The metal framework in cluster compounds is as a rule coated by a dense layer of ligands, both terminal and bridging§, which may consist of individual atoms (H,[32,33] Cl, Br, I,[34-36] S, Se, Te [37,38]), groups of atoms (CR,[39] EL [40]), or molecules (CO,[41,42] NO,[43] olefins, arenes [44-47]), etc. Monoatomic ligands (H, C, N, S, P, etc.) can sometimes be located within the metallic framework surrounded on the outside by other ligands.[48-51] On the other hand, the so-called "ligand-free" metal clusters can exist under specific specially created conditions in both condensed and gas phases in the form of ultradisperse metallic systems[52,53] or "naked" cluster ions.[24]

A profound analogy between cluster compounds of metals and skeletal and polyhedral compounds of non-metallic elements such as boron, phosphorus, arsenic, etc. has been noted.[54] The principle of isolobal correspondence[55] makes it possible, for example, to "substitute" boron atoms in the polyhedron by metal-containing groups with formation of polyhedral metalloboranes[56]—compounds which occupy an intermediate position between the skeletons of non-metallic elements and cluster compounds of metals.

Analysis of the trends in the development of the chemistry of cluster compounds permits the conclusion that for each element in the Periodic System it is probably possible to obtain molecular compounds with frameworks in the form of chains, rings, skeletons, or polyhedra made up of atoms of the given element. In other words, examination of the geometrical structure,[57] electronic structure,[58,59] and the energy relations[60] of the known cluster compounds does not reveal any fundamental factors prohibiting the formation, on the basis of any element of the Periodic System, of molecular compounds having the simplest structural elements specified above. In this sense the chemistry of cluster compounds is the "organic" chemistry of non-carbon elements.

The synthesis,[61] reactivity,[62] electrochemistry,[63,64] dynamics,[65,66] and stereochemistry[67,68] of cluster compounds of metals have been examined in a series of review articles. It has been shown that the coordination of the ligands to several metal centres in the cluster¶ as a rule differs significantly from the coordination of the same ligands in mononuclear complexes.[69,70] In this connection the use of cluster compounds and materials as catalysts, both homogeneous and heterogeneous, constitutes one of the leading trends in research into catalysis.[71-74] Clusters enter into the composition of a new class of biocatalysts—polynuclear oxidation-reduction enzymes (ferredoxins,[75] ferritins,[76] etc.) and play a key role in a series of most important biological processes, such as oxidation,[77] the fixation of atmospheric nitrogen, etc.[78,79]

It has been established that, together with the cluster compounds of metals, many solids (materials) without molecular structure also contain discrete cluster groups made up of metal atoms separated from one another by non-metallic elements (ligands). For example, cluster groups are the principal structural elements of the so-called "Chevrel phases", which are ultraconducting materials with high critical fields;[80,81] chains made up of metal atoms are the principal structural element of quasi-one-dimensional conducting materials;[82] materials of the type "claspol" containing metal clusters in polymer matrices have been produced.[83]

The intermediate position of cluster compounds between the thoroughly investigated mononuclear and coordination compounds, on the one hand, and compact metals, which have been just as thoroughly investigated, on the other, and the fact that they possess a set of properties differing from both the former and the latter[84] necessitates a vigorous development of theoretical ideas concerning the nature of the bonds in cluster molecules.[85-92] However, despite considerable advances, the questions of the electronic structure of cluster compounds are actually the most controversial at the present time†.

In order to deduce the general rules, extensive experimental data are necessary; although the number of cluster compounds which have been isolated and characterised is fairly large, for many types of clusters, in particular those of moderate and high nuclearity, only 1–2 examples are known, as a rule comprising one metal and ligands of one type.[93]

In contrast to this, cluster compounds having a framework in the form of three-membered metallocycles are widely distributed, have been obtained for the majority of metals, and have ligands of different types. Furthermore, in cluster compounds with a high nuclearity most of the faces of the polyhedra in the metal framework are triangular and three-membered metallocycles can therefore model to some extent the properties of more complex clusters. Within the framework of the rule of skeletal electron pairs,[85] the triangle made up of metal atoms is the principal structural element in the group of polyhedra (the tetrahedron, the trigonal bipyramid, etc.), each having 12 skeletal electrons and in this sense, can be regarded as the *nido*-structure in relation to the tetrahedron and the *arachno*-structure in relation to the trigonal bipyramid.[94] Furthermore, a triangle made up of metal atoms is the simplest element of close packing on the surface of certain faces of metallic crystals; here there is also a possibility of modelling properties, in particular in problems of the interaction of adsorbed substrates with the surfaces of metals.[95,96]

Accordingly, the possible relations between the structure of cluster compounds, the number of cluster valence electrons (CVE), the number and nature of the ligands, and the position of the element in the Periodic System are analysed in this review in relation to the widely distributed "simplest" cluster molecules, having a framework made up of three-membered metallocycles, which have been studied in detail. The relevant conclusions are compared with the results of quantum-chemical calculations on the electronic structures of triangular clusters.

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§ In designating the bridging character of a bond, the Greek letter μ is placed before the symbol representing the given ligand; if the number of metal atoms to which the ligand is bound is greater than two, numerical designations are used, for example μ_3-H, μ_4-PPh, etc.

¶ Henceforth cluster compounds will be referred to for brevity as "clusters" and in those cases where it will be necessary to note the properties of clusters as representatives of the class of coordination compounds, we shall employ the term "complexes".

† A detailed critical examination of various approaches to the description of the electronic structure of cluster compounds has been carried out in the review of Yu.L.Slovokhotov and Yu.T.Struchkov (in this issue of the Journal).

II. THREE-MEMBERED METALLOCYCLES HAVING THE "MAGIC" NUMBER OF VALENCE ELECTRONS

The electronic structure of triangular molecular systems has been frequently investigated as the simplest case of cluster interactions. The "magic" number of cluster valence electrons for three-membered metallocycles is 48; here each metal atom at the apex of the triangle assumes the 18-electron configuration.

The absence of bridging ligands and a high symmetry make the trinuclear cluster ruthenium and osmium carbonyls convenient reference compounds for structural, spectroscopic, and theoretical studies on three-membered metallocycles. The $M_3(CO)_{12}$ molecules, where M = Ru or Os, have the structure of an equilateral triangle with D_{3h} symmetry:[97,98] each metal atom is linked to four terminal CO groups; two of these are equatorial and are located in the plane of the ring, while the other two are perpendicular to this plane (Fig.1). The carbonyl groups are almost linear; the deviation of the axial CO groups from linearity is appreciably greater than for the equatorial groups, probably owing to the repulsion of the oxygen atoms of the neighbouring ligands, whose van der Waals radius is greater than that of carbon. The M–C bond lengths also differ somewhat: the axial CO ligands are in the *trans*-positions relative to one another and have longer M–C bonds, while the equatorial CO groups are in the *trans*-position relative to the metal–metal bond and, as a consequence of the π-acceptance, they can shorten somewhat the M–C bond. Overall, 12 CO ligands are distributed in such a way that the resulting ligand polyhedron is an anticubo-octahedron (Fig.1*b*).[94]

The selection rules for the $Os_3(CO)_{12}$ molecule (D_{3h} symmetry space group) predict two vibrational modes for the metal–metal bond: A_1 (fully symmetrical vibration) and E (doubly degenerate vibration). Analysis of the Raman spectra of $Os_3(CO)_{12}$ in the low-frequency range (30–200 cm^{-1}) showed[99] that, among the 12 frequencies active in the Raman spectrum, the two most intense frequencies can be assigned to ν(M–M): A'_1 at 158 cm^{-1} and E' at 117 cm^{-1}; the contribution of the deformations of the M–C bond to the

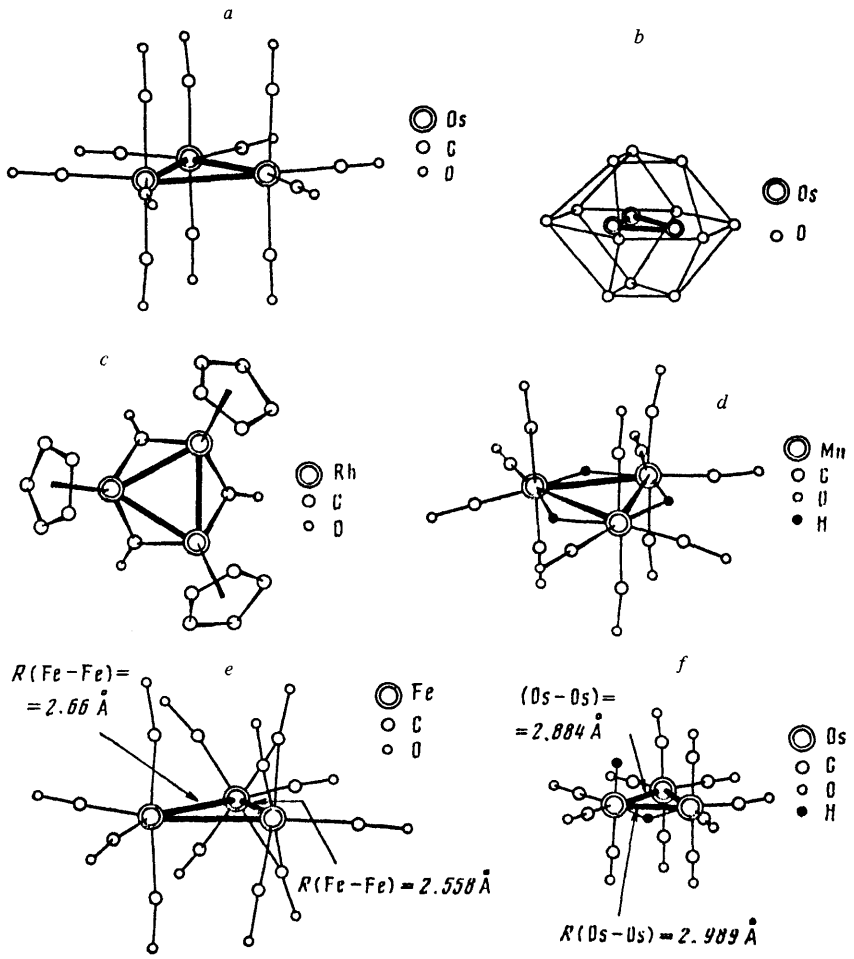

Figure 1. The structure of three-membered metallocycles with 48 CVE and having no μ_3-ligands: *a*) $Os_3(CO)_{12}$; R(Os–Os) = 2.877 Å; R(Os–C_{ax}) = 1.946 Å; R(Os–C_{eq}) = 1.912 Å;[98] *b*) the anticubo-octahedron as the ligand polyhedron of the $M_3(CO)_{12}$ molecule;[94] *c*) $Rh_3(\mu\text{-}CO)_3(Cp)_3$; R(Rh–Rh) = 2.62 Å; R(Rh–C_{Cp}) = 2.24 Å; R(Rh–C_{CO}) = 2.00 Å;[102] *d*) $Mn_3(\mu\text{-}H)_3(CO)_{12}$; R(Mn–Mn) = 3.111 Å; R(Mn–H) = 1.72 Å; R(Mn–C_{ax}) = 1.854 Å; R(Mn–C_{eq}) = 1.789 Å;[101] *e*) $Fe_3(\mu\text{-}CO)_2(CO)_{10}$;[120] *f*) $Os_3(CO)_{11}(\mu\text{-}H)(H)$.[124]

potential energy of these vibrational modes has been estimated at 20% (A_1') and 50% (E'). It is striking that calculation of the force constants for the Os–Os bond yielded two very similar values: $f_{Os-Os} = 0.91 \times 10^{-3}$ dyn A^{-1} when account is taken of the contribution of all the ligands and $f_{Os-Os} = 0.93 \times 10^{-3}$ dyn A^{-1} when no account is taken of the ligands. The analogous calculation for $Ru_3(CO)_{12}$ yielded $f_{Ru-Ru} = 0.82 \times 10^{-3}$ dyn A^{-1} in full agreement with the general tendency towards the weakening of the M–M bond on moving along the Groups of the Periodic System from below upwards. We may also note that $\nu_{A_1'}/\nu_{E'} \cong \sqrt{2}$, which agrees well with the theory for the vibrations of the M_3 triangle as a whole without taking into account the interaction with the ligands.

In the region of the stretching vibration frequencies of the CO ligand (1800–2100 cm^{-1}) the spectra of $M_3(CO)_{12}$, where M = Ru or Os, show absorption bands due solely to the terminal CO ligands;[99] on dissolution, only slight changes take place in the positions and intensities of the CO vibration bands, which indicates the preservation in solution of the principal symmetry elements of these molecules, found for crystalline specimens.

It is possible to detect rapid exchange processes in solutions of the above compounds on the NMR time scale, but the rates of these processes for ruthenium and osmium carbonyls differ very significantly. At 10 °C the ^{13}C NMR spectrum of a solution of $Os_3(CO)_{12}$ consists of two lines (due to the axial and equatorial CO ligands) with a 1 : 1 intensity ratio and corresponds to a structure of this compound in the crystal with D_{3h} symmetry. On heating, the above signals are broadened; the coalescence point is at ~70 °C; at 100 °C a single broad signal corresponding to the positional exchange of the CO ligands (axial–equatorial) is observed.[100] It is striking that in $Ru_3(CO)_{12}$ solutions this type of exchange is observed over the entire experimental temperature range down to −100 °C. Several hypotheses concerning the mechanism of the exchange process have been put forward.[65,66]

Table 1. Three-membered homoelemental metallocycles without μ_3-ligands (48 CVE).

Formula	Refs.
$Mn_3(\mu\text{-H})_3(CO)_{12}$	[101]
$Tc_3(\mu\text{-H})_3(CO)_{12}$	[57]
$Re_3(\mu\text{-H})_3(CO)_{12}$	[57]
$[Re_3(\mu\text{-H})_2(CO)_{12}]^-$	[112]
$[Re_3(\mu\text{-H})(CO)_{12}]^{2-}$	[116]
$Re_3(\mu\text{-H})_3(CO)_{10}(Py)_2$	[118]
$Re_3(\mu\text{-H})_3(CO)_{11}PPh_3$	[119]
$Fe_3(\mu\text{-CO})_2(CO)_{10}$	[103, 120]
$[Fe_3(\mu\text{-H})(\mu\text{-CO})(CO)_{10}]^-$	[121]
$Fe_3(\mu\text{-CO})_2(CO)_9ER_3(E = P, As)$	[122]
$Fe_3(\mu\text{-CO})_2(CO)_7L_3(L = PR_3; P(OR)_3)$	[123]
$Ru_3(CO)_{12}$	[97]
$Ru_3(CO)_{10}L_2$	[57]
$Ru_3(\mu\text{-GeMe}_2)_3(CO)_9$	[57]
$Os_3(CO)_{12}$	[98]
$Os_3(CO)_{11}P(OMe)_3$	[104]
$Os_3(\mu\text{-H})(CO)_{11}(H)$	[124]
$Rh_3(\mu\text{-CO})_3(Cp)_3$	[102]

Tables 1–4 list the main types of the homo- and heteroelement and three-membered metallocycles, each containing 48 CVE. Evidently, the ruthenium and osmium carbonyls examined above are in essence compounds with identical structural characteristics in which the metal-containing fragments are linked to one another by metal–metal bonds. In all the remaining cases there is a certain number of bridging ligands in the ring. Typical examples of the cluster structures listed in Table 1 are illustrated in Fig. 1.

The hydride $Mn_3(\mu\text{-H})_3(CO)_{12}$ has a structure closest to the $M_3(CO)_{12}$ structures, where M = Ru or Os. Six axial and six equatorial CO ligands are linked to the equilateral triangle of Mn atoms.[101] The difference consists only in the fact that three bridging hydrogen atoms are located along the metal–metal bonds in the plane of the triangle#. The rhodium compound $Rh_3(\mu\text{-CO})_3(Cp)_3$ is less symmetrical, although it does possess an idealised threefold symmetry axis; the bridging CO ligands and $\eta^5\text{-}C_5H_5$ groups are located on different sides relative to the equilateral Rh_3 triangle.[102] In the equilateral triangle of Fe atoms in the $Fe_3(CO)_{12}$ molecule, one metal atom has the same geometry (two axial and two equatorial CO ligands) as the metal atoms in $M_3(CO)_{12}$, where M = Ru or Os. However, the other two metal atoms are linked by strongly asymmetric bridges made up of CO ligands.[103] Despite this, the CO ligands are close packed on the surface of the Fe_3 ring and form an idealised cubo-octahedron.[66]

Table 2. Three-membered heteroelemental metallocycles without μ_3-ligands (48 CVE).

Formula	Refs.
$[MnFe_2(\mu\text{-CO})_2(CO)_{10}]^-$	[46]
$[MnOs_2(CO)_{12}]^-$	[46]
$[TcFe_2(\mu\text{-CO})_2(CO)_{10}]^-$	[26]
$[ReFe_2(\mu\text{-CO})_2(CO)_{10}]^-$	[26]
$[ReOs_2(CO)_{12}]^-$	[46]
$Re_2Ru(H)_2(CO)_{12}$	[26]
$MoRh_2(\mu\text{-CO})_2(CO)_5(\eta^5\text{-}C_5Me_5)_2$	[148]
$FeRu_2(CO)_{12}$	[26]
$FeOs_2(CO)_{12}$	[26]
$Fe_2Ru(\mu\text{-CO})_2(CO)_{10}$	[46]
$Fe_2Os(\mu\text{-CO})_2(CO)_{10}$	[26]
$Fe_2Co(\mu\text{-CO})_2(CO)_7Cp$	[26]
$Fe_2Rh(\mu\text{-CO})_2(CO)_7Cp$	[46]
$FeRh_2(\mu\text{-CO})_2(CO)_4(Cp)_2$	[46]
$RuOs_2(CO)_{12}$	[26]
$Ru_2Os(CO)_{12}$	[26]
$Co_2Os(\mu\text{-CO})(CO)_{10}$	[26]

The $Os_3(CO)_{11}(\mu\text{-H})(H)$ cluster is the least symmetrical among those examined above. One axial CO group has been replaced by the H ligand, while the second hydrogen atom is of the bridging type and is located in the equatorial plane. The corresponding Os–Os distance is greater by 0.112 Å than the lengths of the other two Os–Os bonds.[104]

The lengthening of the Mn–Mn bond is typical of clusters where no bridging groups other than μ-H are present along the edge.

Many stable 48-electron three-membered metallocycles are centred on one or two sides on various μ_3-ligands (Tables 3 and 4) in which the key atom can be both a carbon atom and the atoms of other elements. The structures of the most typical compounds of this type are presented in Figs. 2 and 3.

A series of clusters with a μ_3-CR ligand are illustrated in Fig. 2*a* by means of the two most typical examples. In the $Co_3(CO)_9(\mu_3\text{-}CCH_3)$ cluster an sp^3-hybridised carbon atom is located above the three cobalt atoms of the equilateral Co_3 triangle; the three cobalt atoms are linked to it via single Co–C bonds directed at a 60° angle relative to the plane of the triangle. The tetrahedral environment of the carbon atom is somewhat distorted because the Co–C–Co angles are on average only ~80°. All the atoms are electronically and coordinatively saturated, so that the $Co_3(CO)_9CR$ cluster group is always diamagnetic.[105]

The formation of the frontier orbitals of the $Co_3(CO)_9(\mu_3\text{-}CH)$ cluster from the orbitals of the $Co_3(CO)_9$ and CH fragments is shown schematically in Fig. 4, the scheme having been taken from Schilling and Hoffman.[106] The frontier orbitals of the planar $Co_3(CO)_9$ fragment with C_{3v} symmetry have been obtained by adding three electrons to the frontier molecular orbitals of the $Fe_3(CO)_9$ fragment; it is assumed that this does not entail significant changes in the electronic structure except for the alteration of the order of the orbitals with $2a_1$ and $1a_2$ symmetry, which have similar energies. The three orbitals of the CH group are hybridised in such a way that one-low-lying orbital, having an electron pair, is directed towards the side opposite to that of the C–H bond, while the other two orbitals, which are degenerate *p*-type orbitals, are perpendicular to the C–H bond and have one electron. It is striking that the orbital with a_1 symmetry, which is unsuitable for bonding to the group located over the centre of the ring, becomes the highest occupied orbital in the cluster.

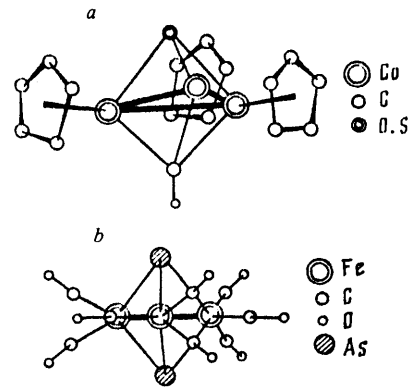

Figure 3. The structure of three-membered metallocycles with 48 CVE each having two μ_3-ligands: *a*) $Co_3(Cp)_3(\mu_3\text{-}CO)(\mu_3\text{-}E)$ [113,114] [E = O: R(Co–Co) = 2.37 Å, R(Co–C_{CO}) = 1.78 Å, R(Co–O) = 2.00 Å; E = S: R(Co–Co) = 2.452 Å]; *b*) $Fe_3(CO)_9(\mu_3\text{-}As)_2$;[115] R(Fe–Fe) = 2.62 Å; R(Fe–C) = 1.80 Å; R(Fe–As) = 2.348 Å.

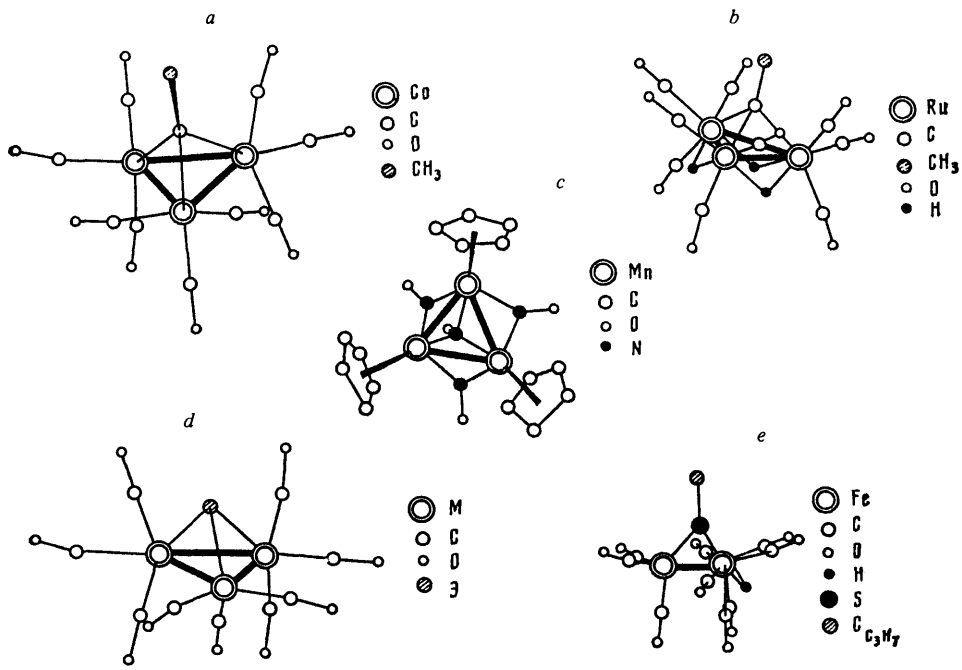

Figure 2. The structure of three membered metallocycles with 48 CVE each having one μ_3-ligand: *a*) $Co_3(\mu_3\text{-}CCH_3)(CO)_9$;[39] R(Co–Co) = 2.467 Å; R(Co–C_{apic}) = 1.90 Å; R(Co–C_{CO}) = 1.80 Å; R(C–CH_3) = 1.53 Å; *b*) $Ru_3(CO)_9(\mu\text{-}H)_3(\mu_3\text{-}CCH_3)$;[127] R(Ru–Ru) = 2.842 Å; R(Ru–C_{apic}) = 2.083 Å; R(Ru–H) = 1.72 Å; *c*) $Mn_3(\mu\text{-}NO)_3(Cp)_3(\mu_3\text{-}NO)$;[108] R(Mn–Mn) = 2.506 Å; R(Mn–N_{μ_3}) = 1.929 Å; R(Mn–N_{μ}) = 1.848 Å; *d*) $FeCo_2(CO)_9(\mu_3\text{-}E)$ [57] [E = S: R(M–M) = 2.55 Å, R(M–E) 2.16 Å; E = Se: R(M–M) = 2.58 Å, R(M–E) = 2.29 Å; E = Te: R(M–M) = 2.60 Å, R(M–E) = 2.47 Å]; *e*) $Fe_3(CO)_9(\mu\text{-}H)(\mu_3\text{-}SC_3H_7\text{-iso})$;[46] R(Fe–Fe) = 2.657 Å; R(Fe–S) = 2.143 Å; R(Fe–H) = 1.80 Å.

Many compounds with the $(CO)_9Co_3C$ fragment, linked to various groups R such as H, halogen, alkyl, arylalkyl, halogenoalkyl, alkoxy, etc., as well as organometallic and other analogous groups are known.[40] The "organic chemistry" of the μ_3-C atom linked to the $Co_3(CO)_9$ fragment has been studied in detail.[39] Tables 3 and 4 show that the μ_3-C bridges are widely distributed in the chemistry of three-membered metallocycles. Fig.2 illustrates the structure of the $Ru_3(CO)_9(\mu\text{-}H)_3(\mu_3\text{-}CCH_3)$ cluster, whose composition differs from that of the cobalt cluster examined above by the presence of three bridging hydrogen atoms; the latter are not located in the plane of the Ru_3 ring, as happens, for example, in the structure of the hydride $Mn_3(\mu\text{-}H_3(CO)_{12}$, but deviate in the direction opposite to that of the side of the metallocycle centred on the μ_3-CCH_3 group. The molecule has approximately the C_{3v} symmetry.[107]

Table 3. Three-membered homo- and hetero-elemental metallocycles each having one μ_3-ligand (48 CVE).

Formula	Refs.
$Co_3(CO)_9(\mu_3\text{-}B\text{-}NEt_2)$	[40]
$Co_3(\mu\text{-}CO)_3(CO)_6(\mu_3\text{-}Al)$	[40]
$Co_3(CO)_9(\mu_3\text{-}CR)$	[39]
$Fe_2(\mu\text{-}CO)_3(Cp)_2(\mu_3\text{-}CR)$	[128]
$FeWPt(\mu\text{-}CO)(CO)_5(PMe_2Ph_2)_2(Cp)(\mu_3\text{-}CR)$	[125]
$Os_3(CO)_9(\mu\text{-}H)_3(\mu_3\text{-}CH)$	[126]
$Os_3(CO)_9(\mu\text{-}H)_3(\mu_3\text{-}CCH_3)$	[46]
$Ru_3(CO)_9(\mu\text{-}H)_3(\mu_3\text{-}CCH_3)$	[127]
$Fe_2Ni(CO)_7(Cp)(\mu_3\text{-}CCH_2CH_3)$	[26]
$Co_2W(CO)_8(Cp)(\mu_3\text{-}CC_6H_4CH_3)$	[130]
$Ni_3(Cp)_3(\mu_3\text{-}CC_6H_5)$	[129]
$FeRhW(\mu\text{-}CO)(CO)_5(Cp)(\eta^5\text{-}C_9H_7)(\mu_3\text{-}CC_6H_4CH_3)$	[125]
$Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}NC_6H_5)$	[131]
$Ru_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}NC_6H_5)$	[132]
$Fe_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}NSiMe_3)$	[133, 134]
$Mn_3(\mu\text{-}NO)_3(Cp)_3(\mu_3\text{-}NO)$	[108]
$Ir_3(PF_3)_9(\mu_3\text{-}P)$	[135]
$CO_8(CO)_9(\mu_3\text{-}PS)$	[129]
$Fe_2Cr(\mu\text{-}CO)_2(CO)_9(\mu_3\text{-}PC_6H_5)$	[26]
$Fe_2Mn(\mu\text{-}CO)_2(CO)_6(Cp)(\mu_3\text{-}PC_6H_5)$	[136]
$Ru_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}S)$	[129]
$Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}S)$	[57]
$FeCo_2(CO)_9(\mu_3\text{-}S)$	[57]
$FeCo_2(CO)_9[\mu_3\text{-}S\text{-}Cr(CO)_5]$	[111]
$Fe_3(CO)_9(\mu\text{-}H)(\mu_3\text{-}SR)$	[46]
$Ru_3(CO)_9(\mu\text{-}H)_2(\mu_3\text{-}Se)$	[129]
$FeCo_2(CO)_9(\mu_3\text{-}Se)$	[57]
$Ru_3(CO)_9(\mu\text{-}H)_2(\mu_3\text{-}Te)$	[129]
$FeCo_2(CO)_9(\mu_3\text{-}Te)$	[57]
$Re_3(\mu\text{-}H)_3(CO)_9(\mu_3\text{-}SBu\text{-}t)$	[137]

Clusters with NO ligands are so far comparatively rare (see, for example, Feltham and Enemark[43]). Fig.2*c* illustrates the structure of the compound $Mn_3(\mu\text{-}NO)_3(Cp)_3.(\mu_3\text{-}NO)$.[108] The molecule has the C_{3v} symmetry; in its base is located the equalateral Mn_3 triangle, each side of which is spanned by a bridging NO group which is not located in the plane of the ring: the deviation of the NO group from the plane of the ring is ~47°. On the opposite side, the ring is centred on the μ_3-NO ligand. The planar Cp rings deviate from the plane of the triangle by an angle of ~17° towards the side opposite to that of the μ-NO ligands. Overall, this arrangement results in a fairly close symmetrical packing of the ligands around the Mn_3 triangle.

The centering of the three- and four-carbon faces in clusters with a high nuclearity on chalocogenide ligands is very common; three-membered metallocycles with μ_3-chalcogenide ligands are therefore of special interest. Fig.2*d* presents the structures of the most typical representatives of these compounds. The structure of the clusters $Co_2Fe(CO)_9(\mu_3\text{-}X)$, where X = S, Se, or Te, are isotypical; the molecules have approximately the C_{3v} symmetry, and one of the sides of the Co_2Fe ring is centred on the X group; the ring is in essence an equalateral triangle. The differences in the M–M bond length are within the limits of the accuracy of the method, which is not surprising bearing in mind that the covalent radii of the Fe and Co atoms are virtually identical (1.165 and 1.162 Å).[109,110] Fig.2 shows that the metal–metal distances depend on the nature of the chalogen and increase with the increase of the radius or the μ_3-X group. We may note that the chalcogen atom in the μ_3-arrangement provides only four electrons for the formation of bonds with the metal atoms; it retains a free electron pair located in an orbital directed to the "outside" at right angles to the plane of the ring. It can be detected experimentally: such clusters behave like the usual two-electron-donating ligands and are capable, for example, of substituting the CO group in chromium carbonyl with formation of a derivative of the usual type—cyclo-$FeCo_2(CO)_9[\mu_3\text{-}S.Cr(CO)_5]$.[111]

Table 4. Three-membered homo- and hetero-elemental metallocycles each having two μ_3-ligands (48 CVE).

Formula	Refs.
$Ru_3(CO)_9(\mu_3\text{-}CO)[\mu_3\text{-}NSi(CH_3)_3]$	[46]
$Fe_3(CO)_9(\mu_3\text{-}CO)[\mu_3\text{-}NSi(CH_3)_3]$	[133]
$Co_3(Cp)_3(\mu_3\text{-}CO)[\mu_3\text{-}NSi(CH_3)_3]$	[46]
$Rh_3(Cp)_3(\mu_3\text{-}CO)[\mu_3\text{-}NSi(CH_3)_3]$	[46]
$Co_3(Cp)_3(\mu_3\text{-}CO)(\mu_3\text{-}N\text{—}N{=}CPh_2)$	[138]
$Co_3(Cp)_3(\mu_3\text{-}CO)(\mu_3\text{-}S)$	[114]
$Co_3(Cp)_3(\mu_3\text{-}CO)(\mu_3\text{-}O)$	[113]
$Ni_2Co(Cp)_3(\mu_3\text{-}CO)_2$	[26]
$Ni_2Fe(Cp)_2(CO)_5(\mu_3\text{-}CO)_2$	[26]
$[Ni_2Mn(Cp)_2(CO)_3(\mu_3\text{-}CO)_2]^-$	[26]
$Co_3(Cp)_3[\mu_3\text{-}CN(C_2H_5)_2]_2$	[126]
$Rh_3(Cp)_3[\mu_3\text{-}CN(C_2H_5)_2]_2$	[126]
$Co_3(Cp)_3(\mu_3\text{-}NO)_2$	[43]
$Fe_3(CO)_9(\mu_3\text{-}As)_2$	[115]
$Fe_3(CO)_9[\mu_3\text{-}SnFe(CO)_2(Cp)]_2$	[57]

In contrast to this, the μ_3-SR group (where R is an organic substituent) provides five electrons for the formation of bonds with metal atoms. Fig.2*e* illustrates the structure of the cluster compound $Fe_3(CO)_9(\mu\text{-}H)(\mu_3\text{-}SC_3H_7\text{-iso})$; the Fe atoms form an almost equilateral triangle, the bridging hydride being directed to the side opposite to that of the μ_3-SR group and linking symmetrically two Fe atoms.[112]

The centering of the three-membered rings on the μ_3-ligands on two sides renders the ligand shells in such cluster molecules more compact and probably increases their stability. Examples of triangular clusters with two μ_3-ligands are presented in Table 4; certain structures are illustrated in Fig.3.

The centering of the triangular face on μ_3-CO ligands is frequently observed in cluster compounds with high nuclearity; such examples are encountered much more rarely among the triangular clusters considered in this review. A rare structurally characterised example of the coordination of the oxygen atom as a μ_3-ligand, which provides four electrons for the formation of bonds with metal atoms, occurs in the $Co_3Cp_3(\mu_3\text{-}CO)(\mu_3\text{-}O)$ cluster. Owing to the small radius of the oxygen atom, the principal Co–O, Co–Co, and Co–C_{CO} bond lengths in the molecule are somewhat shortened.[113]

This can be seen fairly clearly from a comparison of the corresponding distances in the isoelectronic and isostructural cluster $Co_3Cp_3(\mu_3\text{-}CO)(\mu_3\text{-}S)$,[114] in which the Co–Co bond length is greater almost by 0.1 Å.

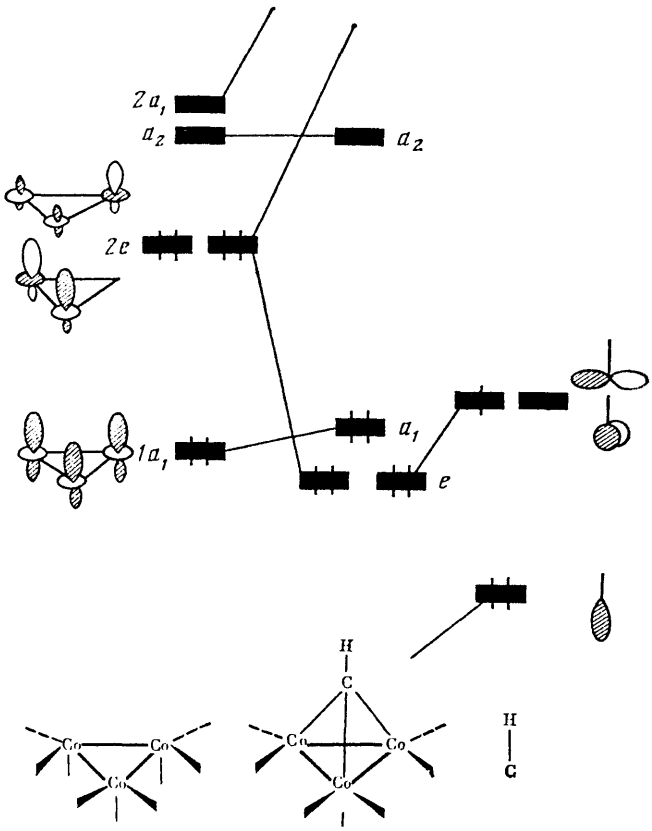

Figure 4. The frontier orbitals of the $Co_3(CO)_9(\mu_3\text{-}CH)$ cluster.[106]

Finally in the last of the structures considered (Fig. 3*b*), namely that of the $Fe_3(CO)_9(\mu_3\text{-}As)_2$ cluster, each of the two arsenic atoms behaves as a three-electron ligand and the Fe_3 triangle is centred on them on two sides.[115]

Thus three-membered metallocycles, each having 48 CVE, are fairly common; the homometallic compounds are characteristic of transition elements with the d^7–d^9 electronic configuration; in heterometallic clusters the range of elements is wider—they can incorporate Pt(d^{10}), W, or Cr(d^6). The metal framework in cluster compounds of this type can be surrounded by ligands differing significantly in both their electronic and steric properties. The majority of the cluster compounds presented in Tables 1–4 possess π-acceptor linear carbonyl ligands; together with these, π-donor ligands are also present, namely ligands such as S, Cp, Sr, NR, etc., as well as ligands incapable of additional π-interaction with the metal framework, of the type of CR, B-NEt_3, etc.

It is noteworthy that Tables 1–4 list clusters without CO ligands, for example, $Co_3Cp_3(\mu_3\text{-}NO)_2$ and $Rh_3Cp_3[\mu_3\text{-}CN.(C_2H_5)_2]_2$, as well as the $Ir_3(PF_3)_9(\mu_3\text{-}P)$ cluster in which there are no M–C bonds at all. A definite preference for either ligands or metals in the formation of compounds of this type should probably not be expected. The existence of a large number of cluster compounds with carbonyl ligands, which have been synthesised and investigated, is not due to their special properties but apparently arises because in the initial stages of the development in this field metal carbonyls were most often employed as the starting compounds in the synthesis of clusters.

Table 5. Three-membered metallocycles each having 49 CVE.

Formula	Refs.
$Co_3(CO)_9(\mu_3\text{-}S)$	[109]
$Co_3(CO)_9(\mu_3\text{-}Se)$	[110]
$Ni_3(Cp)_3[\mu_3\text{-}NC(CH_3)_3]$	[139]
$Co_3(CO)_9(\mu_3\text{-}PR)$	[46]
$Ni_3(Cp)_3(\mu_3\text{-}CO)_2$	[57]
$[Co_3(Cp)_3(\mu_3\text{-}S)_2]^+$	[114]

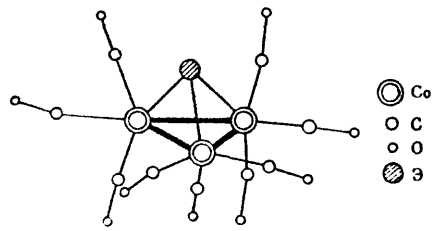

Figure 5. The structure of the $Co_3(CO)_9(\mu_3\text{-}E)$ clusters;[109,110] E = S: R(Co–Co) = 2.64 Å, R(Co–E) = 2.14 Å; E = Se: R(Co–Co) = 2.62 Å, R(Co–E) = 2.28 Å.

III. TRIANGULAR CLUSTERS WITH AN EXCESS OF VALENCE ELECTRONS

Several examples of entirely stable structurally characterised triangular metallocycles containing more than the magic number of valence electrons are known. Examples of such compounds are presented in Table 5. It is striking that they all have at least one μ_3-ligand.

In the first place we shall consider paramagnetic compounds, each having 49 CVE. The structure of the $Co_3(CO)_9(\mu_3\text{-}E)$ clusters, where E = S or Se [109,110] (Fig. 5), is based, like that of the diamagnetic 48-electron analogues $Co_2Fe(CO)_9.(\mu_3\text{-}E)$, where E = S or Se, on an equilateral triangle made up of metal atoms and centred on an apical chalcogenide ligand in accordance with a tetrahedral motif. The molecules have the idealised C_{3v} symmetry. The larger radius of the selenium atom compared with that of the sulphur atom increases the Co–E distance, but hardly affects the length of the Co–Co bond. However, it has been noted[110] that the metal–metal distances in the 49-electron clusters are greater (by 0.08 Å for E = S and 0.04 Å for E = Se) than in the isostructural 48-electron clusters $Co_2Fe(CO)_9(\mu_3\text{-}E)$, where E = S or Se. Consequently the appearance of an unpaired electron entails an appreciable increase of the metal–metal bond length. It has been concluded[110] that the highest

half-filled MO in the $Co_3(CO)_9(\mu_3\text{-}E)$ cluster, where E = S or Se, has a strongly antibonding character in relation to the metal–metal bonds of the Co_3 triangle.

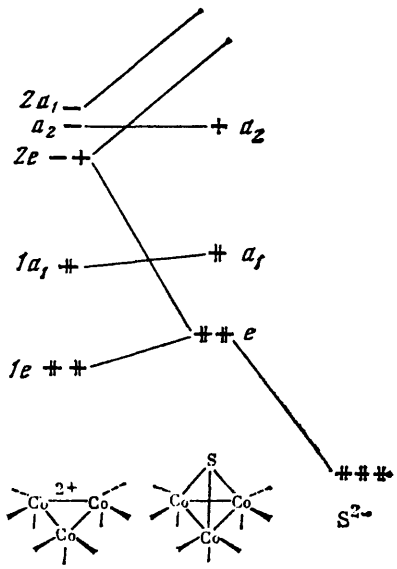

Figure 6. Diagram illustrating the interaction of the orbitals in the formation of the $Co_3(CO)_9(\mu_3\text{-}S)$ cluster.[106]

Fig. 6 illustrates a scheme for the construction of the frontier molecular orbitals of the $Co_3(CO)_9(\mu_3\text{-}S)$ cluster from the orbitals of the $[Co_3(CO)_9]^{2+}$ and S^{2-} fragments.[106] The low-lying fully occupied *p* orbitals of the S^{2-} group interact strongly with the 1*e* orbitals of the $[Co_3(CO)_9]^{2+}$ fragment and conversely the $1a_1$ and a_2 orbitals hardly undergo a change in their positions on formation of the cluster. Apparently the unpaired electron is located in the a_2 orbital of the cluster, which is antibonding in relation to the metal–metal bonds (Fig. 6). Calculations have shown that, when an electron enters this orbital, the overlap populations between the cobalt atoms diminish by a factor greater than 2, which in fact leads to the observed increase of the metal–metal distance.

More detailed experimental information about the nature and spatial orientation of this orbital has been obtained from EPR spectra;[110] the spectra of both solutions of the $Co_3(CO)_9.(\mu_3\text{-}E)$ clusters, where E = S or Se, and the single crystals of the diamagnetic isostructural compounds $FeCo_2(CO)_9(\mu_3\text{-}E)$, containing 0.5% of the isomorphous paramagnetic $Co_3(CO)_9.(\mu_3\text{-}E)$ clusters, have been investigated. The EPR spectrum of a single crystal with E = Se consists of 22 lines due to the hyperfine interactions of the unpaired electron with the three ^{59}Co nuclei ($J = 7/2$). Detailed analysis of the EPR spectra[110] showed that the unpaired electron is located in the non-degenerate antibonding MO disposed in the plane of the Co_3 triangle and made up predominantly of the $3d_{xz}$ orbitals of the Co atom without an appreciable contribution by the *s* orbitals. The hyperfine splitting constant $[A_{11}] = 77.0$ G calculated on this basis is in good agreement with the experimental value $[A_{11}] = 74.3$ G. The hyperfine splitting constant for the $Co_3(CO)_9(\mu_3\text{-}S)$ cluster is smaller by only 2%, i.e. $[A_{11}] = 72.8$ G, than for the selenium compound, which undoubtedly demonstrates yet again the strongly antibonding character of the a_2 orbital and its location in the plane of the ring orthogonally in relation to the *s*, *p*, and *d* orbitals of the apical chalcogen atom.

The compound $Cp_3Ni_3(\mu_3\text{-}S)_2$ [159] having 53 CVE also belongs to the group of paramagnetic triangular clusters. Here the Ni–Ni distances have been increased to 2.80 Å. The stability of the cluster is determined by the density of the ligand packing and the two μ_3-S bridges spanning the metal atoms. The same causes are apparently responsible for the stability of the analogous cobalt cluster $Co_3Cp_3(\mu_3\text{-}S)_2$, which has three electrons less; the Co...Co distances have likewise been increased, to 2.687 Å.[114]

If the μ_3-bridges spanning the metal atoms to form a triangle cannot be formed for one reason or another under the conditions of the synthesis, the presence of 50 CVE in the molecule leads to the rupture of one M–M bond and the conversion of the framework of the cluster from a metallocycle into a metallochain; as a rule, this is not a linear chain but a "wedge" with the angle at the central atom in the range 80–100°; as it were, a slightly open triangle is obtained. A detailed discussion of such molecules is outside the framework of this review.

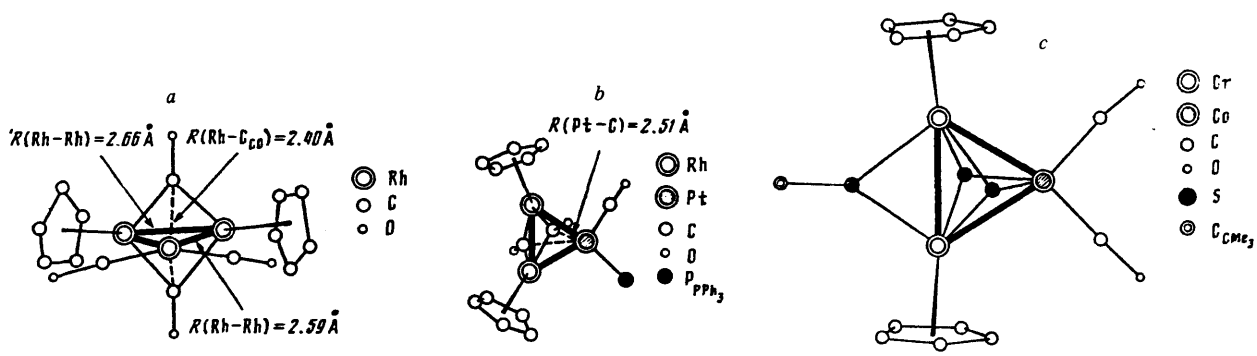

Figure 7. The structure of clusters each having 46 CVE: *a*) $Rh_3(\mu\text{-}CO)_2(CO)_2(Cp)_2$;[144] *b*) $Rh_2Pt(\mu\text{-}CO)_2(CO)(Cp)_2(PPh_3)$;[142] $R(Rh–Rh) = 2.65$ Å; $R(Rh–Pt) = 2.65$ Å; *c*) $Cr_2Co(Cp)_2(CO)_2[\mu\text{-}SC(CH_3)_3](\mu_3\text{-}S)_2$;[143] $R(Cr–Cr) = 2.62$ Å; $R(Cr–Co) = 2.59$ Å; $R(Co–S) = 2.20$ Å; $R(Cr–S_{\mu_3}) = 2.30$ Å.

IV. STABLE THREE-MEMBERED METALLOCYCLES WITH A DEFICIENCY OF VALENCE ELECTRONS

Analysis of structurally characterised triangular clusters has shown that three-membered metallocycles with less than 48 CVE are encountered no more rarely than clusters with the magic number of CVE. In order to discover the cause of the stability of such compounds, we shall examine in greater detail their abundance and the characteristics of their structure.

1. Three-Membered Metallocycles having 46 CVE

Table 6 presents examples of triangular clusters, each having 46 CVE. The homoelemental compounds are represented by rhodium clusters, but most of the compounds are heterometallic clusters each containing two metal atoms with the d^7–d^9 configuration and one Pt atom. In all cases the molecules contain bulky phosphine or Cp ligands together with the CO groups.

Table 6. Homo- and hetero-elemental three-membered metallocycles each having 46 CVE.

Formula	Refs.
$Rh_3(\mu\text{-}PPh_2)_3(CO)_5$	[140]
$Rh_3(\mu\text{-}PPh_2)_3(CO)_3(PPh_3)_2$	[141]
$[Rh_3(\mu\text{-}CO)_2(CO)_2(Cp)_2]^-$	[144]
$Mo_2Fe(Cp)_2(CO)_8$	[26]
$Cr_2Co(Cp)_2(CO)_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2$	[143]
$PtFeW(CO)_6(\mu_3\text{-}CR)(Cp)(PEt_3)$	[125]
$Pt_2W[\mu\text{-}C(OMe)Ph](CO_6[P(t\text{-}Bu)_2)Me]_3$	[57]
$PtFe_2(CO)_8(PR_3)_2$	[125]
$PtFe_2(CO)_9(PR_3)$	[145]
$PtFe_2(CO)_8COD$	[125]
$PtCo_2(CO)_7L_2$	[46, 146]
$PtRu_2(CO)_8(diphos)$	[125]
$PtOs_2(CO)_7(PMePh_2)_3$	[26]
$PtRu_2(CO)_7(PPh_3)_3$	[26]
$PtRh_2(\mu\text{-}CO)_2(COD)(\eta^5\text{-}C_5Me_5)_2$	[142]
$PtRe_2(\mu\text{-}H)_2(CO)_9(PRh_3)$	[26]
$AuRe_2(\mu\text{-}H)(CO)_9(PPh_3)$	[26]
$PtRh_2(\mu\text{-}CO)(\mu_3\text{-}CO)(PPh_3)(\eta^5\text{-}C_5Me_5)_2$	[142]

The cluster species $[Rh_3(\mu\text{-}CO)_2(CO)_2Cp_2]^-$ and $Rh_2Pt.(\mu\text{-}CO)_2(CO)Cp_2(PPh_3)$ can be regarded as the products of the addition of the isoelectronic groups $[Rh(CO)_2]^-$ and $Pt(CO)PPh_3$ to the double bond of the dimer $Cp_2Rh_2(\mu\text{-}CO)_2$ (Figs. 7*a* and 7*b*). Both structures have definite features in common: the CO bridging ligands are not in the same plane with the rhodium atoms in both cases and are inclined in the direction of the third metal atom, so that, for example, the angle between the Rh(1)–Rh(2)–C(5) plane and the plane of the ring is 77.5°; an analogous situation has been observed in a Pt cluster (Fig. 7).

Formally the same result, i.e. the presence of 46 CVE, can be achieved when the framework of the cluster contains one metal atom with the d^8–d^9 configuration and two metal atoms with the d^6 configuration, the structure of one such compound being illustrated in Fig. 7*c*. This is also a product of addition, in this instance of the $Co(CO)_2$ fragment, to a dimeric chromium complex; it is believed[143] that the high exchange interaction parameter ($-2J = 530$ cm^{-1}) is satisfactorily correlated with the shortening of the Cr–Cr distance (2.617 Å).[143] Fig. 7*c* shows that the Cr_2Co triangle is surround by a shell of adjoining ligands; whereby a more complete shielding of the metallic framework against the possible (under the conditions of synthesis) attachment of additional ligands is apparently achieved.

We may note that the appearance of the 47th electron in the cluster $Cr_2Fe(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2(CO)_3$ with an analogous composition leads to a significant "loosening" of one Fe–Cr bond in the triangle (the distances are 2.726 and 3.010 Å respectively).[160]

Furthermore, 46-electron clusters can also be achieved when the triangle contains two Pt atoms and one W atom[57] and also three different atoms (Pt, Fe, and W).[125] The number of such combinations is likely to become fairly large in the future.

2. Three-Membered Metallocycles having 44 CVE

The decrease of the number of CVE in triangular cluster compounds is achieved in two ways—by a gradual accumulation in the framework of atoms of elements lying to the right or to the left of metals with the d^8 electronic configuration. The homoelemental cluster compounds each containing 44 CVE are represented by the Pd and Pt as well as Ir triangular metallocycles (Table 7). The 42-electron triangles considered in the next subsection, are typical for the first two elements; sometimes the reversible addition of yet another two-electron ligand with formation of 44-electron three-membered metallocycles is possible.[161] The very fact of the existence of the equilibrium of the type $Q_{42}CVE + L \rightleftharpoons Q_{44}CVE$ shows that the number of CVE is not the only factor determining the stability of cluster compounds of this type.

Table 7. Homo- and hetero-elemental three-membered metallocycles each having 44 CVE.

Formula	Refs.
$Cr_2Fe(\mu\text{-}OR)_2(CO)_4(Cp)_2$	[149]
$Mo_2Pt(CO)_4(Cp)_2(PPh_3)_2$	[125]
$[Ir_3(H)_6(\mu\text{-}H)\{P(C_6H_{11})_3\}_3Py_3]^{2+}$	[57]
$Pt_2Fe(CO)_8[P(OPh)_3]_3$	[57]
$Pt_2Ru(CO)_5(PR_3)_3$	[147]
$Pt_2Ru(CO)_4(PR_3)_4$	[26]
$Pt_2Os(CO)_5(PR_3)_3$	[26]
$Pt_2Cr[\mu\text{-}C(OMe)Ph](CO)_6(PR_3)_2$	[150]
$Pt_2W[\mu\text{-}C(OMe)Ph](CO)_6(PR_3)_2$	[150]
$Pt_3(\mu\text{-}CO)_3(PR_3)_4$	[57]
$[Pt_3(CO)_3(\mu\text{-}CO)_3]^{2-}$	[57]
$Pd_3[CNC(CH_3)_3]_5(\mu\text{-}SO_2)_2$	[57, 46]
$Pd_3(\mu\text{-}CO)_3(PPh_3)_4$	[46]

Heterometallic triangular clusters are presented in Table 7. A characteristic example of such compounds is the $Pt_2W.[\mu\text{-}C(OMe)Ph])CO)_6[P(t\text{-}Bu)_2Me]_2$ cluster, whose structure is illustrated in Fig. 8*a*. The Pt_2W triangle is equilateral; the planar carbene ligand lies in a plane perpendicular to that of the Pt_2W ring and passing through the W atom and the centre of the Pt–Pt bond; the CO ligands are of the semi-bridging type with markedly different distances to the Pt and W atoms; overall, the metallic framework of the cluster is strongly shielded against external influences by virtue of the branched ligand environment.

If is of interest to compare the structures of two clusters—$FeCr_2(\mu\text{-}OR)_2(CO)_4(Cp)_2$ and $FePt_2(CO)_5[P(OPh)_3$ (Figs. 8*b* and 8*c*). Both compounds contain the electronically saturated $Fe(CO)_4$ group symmetrically linked to the corresponding bimetallic fragments. Evidently, formally the same result (44 CVE) can be achieved via two significantly different pathways. The qualitative schemes for the distribution of electrons among the MO in the clusters indicated have been examined by Eremenko et al.[149] and Johnson and Benfield[94] respectively. The fact that both the Fe atom in the $Fe(CO)_4$ group and the M–M bonds opposite it are strongly sterically shielded owing to the close packing of branched ligands, which is clearly seen from a projection of the structure of the cluster illustrated in Fig. 8*d*, is striking.

One must note that, although the majority of the triangular metallocycles presented in Table 7 contain CO groups as ligands, there exists an example of a cluster compound without CO ligands, namely $Pd_3[CNC(CH_3)_3]_5(SO_2)_2$ [155] as well as a cluster which altogether lacks M–C bonds, namely $\{Ir_3(H)_6 .(\mu\text{-}H)[P(C_6H_{11})_3]_3Py_3\}^{2+}$. [57]

3. Three-Membered Metallocycles having 42 CVE

Table 8 presents examples of cluster compounds which each have 42 CVE; evidently these compounds can be divided into two groups—the cluster compounds of Group VI and VII transition elements and the larger group of platinum, palladium, and rhodium compounds. Fig. 9 illustrates the structures of some of the cluster compounds having 42 CVE each.

The cluster cation $[Mo_3(Cp)_3(\mu\text{-}S)_2(\mu_3\text{-}S)]^+$ is very compact; one side of the Mo_3 triangle is shielded by the μ_3-S ligand, while the other is shielded by three μ-S groups, which deviate markedly from the plane of the ring; from the outside, each Mo atom is coordinated to a planar Cp ring (Fig. 9*a*). On the other hand, the formation of a stable 42-electron platinum cluster apparently does not require the complete shielding of the metallic triangle by a close-packed ligand shell; it is sufficient that the bulky substituents should prevent the mutual approach of the two Pt_3 rings, along the three-fold axis passing through the centre of the ring, to distances sufficient for the formation of prismatic structures with weak metal–metal bonds between the rings.

Table 8. Three-membered metallocycles each having 42 CVE.

Formula	Refs.
$[Re_3(\mu\text{-}Cl)_3Cl_9]^{3-}$	[151]
$[W_3(\mu_3\text{-}O)(\mu\text{-}OAc)_6(H_2O)_3]^{4+}$	[152]
$[Mo_3(\mu\text{-}S)_3(\mu_3\text{-}S)(Cp)_3]^+$	[156]
$Pt_3[\mu\text{-}CNC(CH_3)_3]_3[CNC(CH_3)_3]_3$	[154]
$Pt_3(\mu\text{-}CO)_3(PR_3)_3$	[46]
$Pt_3[\mu\text{-}C(OCH_3)C_6H_4CH_3]_3(CO)_3$	[157]
$Pt_3[\mu\text{-}C(OCH_3)C_6H_5]_3[P(CH_3)_3]_3$	[157]
$Pt_3(H)_6[P(Bu\text{-}tper)_3]_3$	[153]
$Pd_3(\mu\text{-}CO)_3(PPh_3)_3$	[46]
$Rh_3(\mu\text{-}H)_3[P(OCH_3)_3]_6$	[158]

A typical example of such compounds is illustrated in Fig. 9*c*. Each platinum atom has one terminal CO ligand and is linked to its neighbours by a bridging carbene ligand; the carbene ligands are almost planar and each such plane is

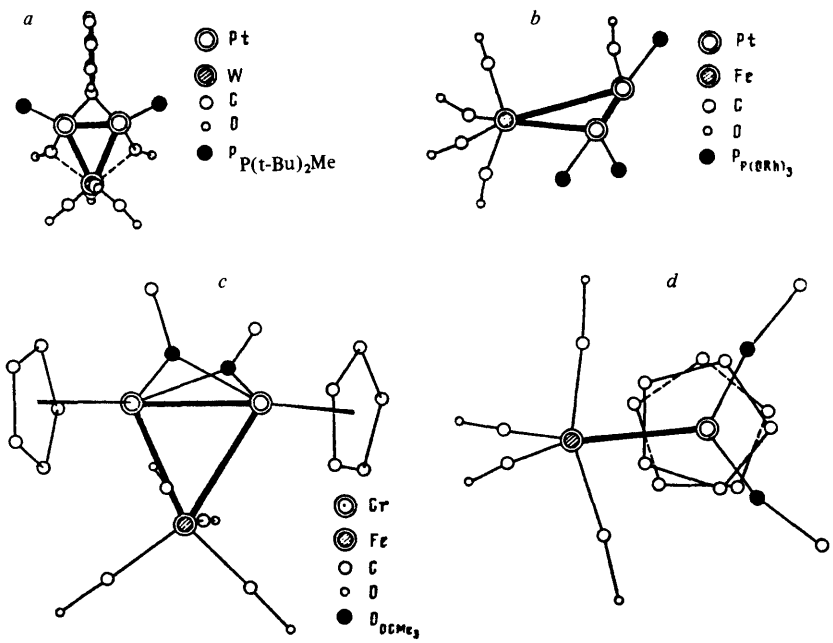

Figure 8. The structure of clusters each having 44 CVE: *a*) $Pt_2W[\mu\text{-}C(OCH_3)C_6H_5](\mu\text{-}CO)_2(CO)_4\{P[C(CH_3)_3]_2CH_3\}_2$;[150] R(Pt–Pt) = 2.63 Å; R(Pt–W) = 2.83 Å; R(Pt–C_{CO}) = 1.87 Å; R(W–C_{CO}) = 2.43 Å; α-(Pt–C–O) = 148°; *b*) $Pt_2Fe(CO)_5[P(OC_6H_5)_3]_3$;[57] R(Pt–Pt) = 2.63 Å; R(Pt–Fe) = 2.57 Å; *c*) $Cr_2Fe[\mu\text{-}OC(CH_3)_3]_2(CO)_4(Cp)_2$;[149] R(Cr–Cr) = 2.64 Å; R(Cr–Fe) = 2.70 Å; *d*) projection along the Cr–Cr axis.

perpendicular to that of the Pt_3 ring and passes through the centre of the Pt–Pt bond.

The only 42-electron rhodium cluster listed in Table 8 is an example of a compound in which the electronically unsaturated metallic triangle is fully shielded by highly branched ligands (Fig. 9*b*). The Rh–Rh distance is increased owing to the presence of the bridging hydrogen atoms.

One must note that, among the three-membered metallocycles listed in Table 8, there are many examples of compounds without M–C bonds: here we encounter for the first time triangular clusters having only typical acido-ligands, which are characteristic of "inorganic" complexes. As an example, we shall consider the $Re_3(\mu\text{-}Cl)_3Cl_9$ cluster, whose structure is illustrated in Fig. 9*d*. Evidently the Re–Re distances are greatly diminished compared with, for example, the length of this bond in $Re_2(CO)_{10}$ (3.02 Å). It has been suggested that multiple M–M bonds are present in this and analogous compounds.[162]

It is striking that the chloride ligands in the above cluster compounds, like the carbonyl groups in compounds of the type $M_3(CO)_{12}$, where M = Ru or Os, give rise to a close-packed configuration and a ligand polyhedron analogous to that shown in Fig. 1 with the sole difference that the central hexagon has been rotated by an angle of 60° relative to the axis passing through the centre of the Re_3 triangle.

The question whether three-membered metallocycles having less than 42 CVE can exist should apparently be answered in the affirmative. The organometallic compound $Re_3(CH_3)_9$, containing 30 CVE and the product of the addition to the latter of phosphine ligands, namely $Re_3(CH_3)_9(PEt_2Ph)_3$, which has 36 CVE, are known.[163]

Thus the following conclusions characterising the relation between the structure and the number of CVE in triangular cluster compounds can be drawn from the data examined above:

1. Stable three-membered cluster compounds of transition metals with the d^6–d^{10} configuration and 48, 46, 44, 42, or fewer CVE are known. The close packing of the bulky ligands on the surface of the metallic framework, which results in the shielding of the M–M bond against the influence of external agents, becomes increasingly pronounced with decrease of the number of CVE.
2. No specific ligand preference in the formation of triangular cluster compounds has been discovered; among the examples listed in Tables 1–8, ligands of virtually all known types are encountered.
3. The smaller the number of CVE in the compound, the shorter the M–M bond; this conclusion is valid for metals with the d^6–d^7 configuration but does not extend to the triangular Pd and Pt clusters.
4. In the cluster compounds with 49 CVE the unpaired electron is located in a highly antibonding (in relation to the M–M bond of the metallic framework) non-degenerate MO. Such compounds have at least one μ_3-bridging ligand, which maintains the metal atoms at short distances from one another.
5. In cluster compounds with 50 CVE a second electron enters the antibonding non-degenerate MO, which leads to the rupture of one metal–metal bond; the triangle is opened and the metallic framework assumes the form of a bent chain made up of three metal atoms.
6. In a cluster having 53 CVE all three Ni...Ni bonds are greatly extended compared with the normal Ni–Ni distance. The stability of such a cluster is determined by the close packing of the ligands in the presence of two μ_3-S bridges spanning the metal atoms.
7. The presence in the cluster framework of each Pt, Pd, and Au atom as a rule reduces the number of CVE by two. A typical number of CVE in the triangle of Pt or Pd atoms is 42 (sometimes 44). In the presence of a greater number

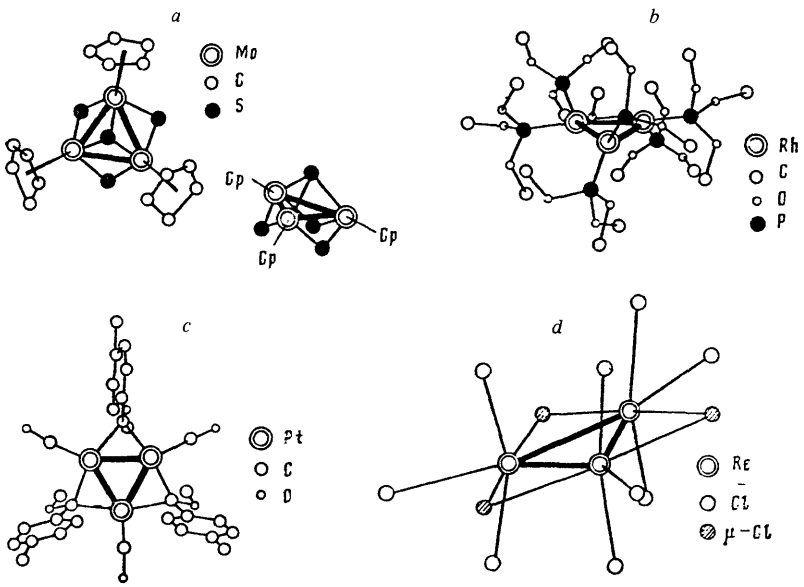

Figure 9. The structure of clusters each having 42 CVE: *a*) $[Mo_3(\mu\text{-}S)_3(\mu_3\text{-}S)(Cp)_3]^+$;[156] R(Mo–Mo) = 2.81 Å; R(Mo–S_μ) = 2.29 Å; R(Mo–S_{μ_3}) = 2.31 Å; *b*) $Rh_3(\mu\text{-}H)_3[P(OCH_3)_3]_6$;[158] R(Rh–Rh) = 2.82 Å; *c*) $Pt_3[\mu\text{-}C(OCH_3)C_6H_4CH_3\text{-}p]_3(CO)_3$;[157] R(Pt–Pt) = 2.62 Å; *d*) $[Re_3(\mu\text{-}Cl)_3Cl_9]^{3-}$; R(Re–Re) = 2.47 Å.[151]

of CVE the homometallic triangle made up of Pt or Pd atoms is open.

V. THE ELECTRONIC STRUCTURE OF THREE-MEMBERED METALLOCYCLES

In the formation of a metallocycle with a framework in the form of a regular triangle the three transition metal atoms each provide nine orbitals ($5d + 1s + 3p$), which results in a set of 27 MO (Fig.10); three of these (a_2' and e') have unduly high energies and are unsuitable for bonding.[164] Consequently in the metallic triangles there are only 24 cluster valence molecular orbitals (CVMO). In the three-membered metallocycles considered this set of MO is occupied in different ways by the electrons provided by the metal atoms and the ligands.

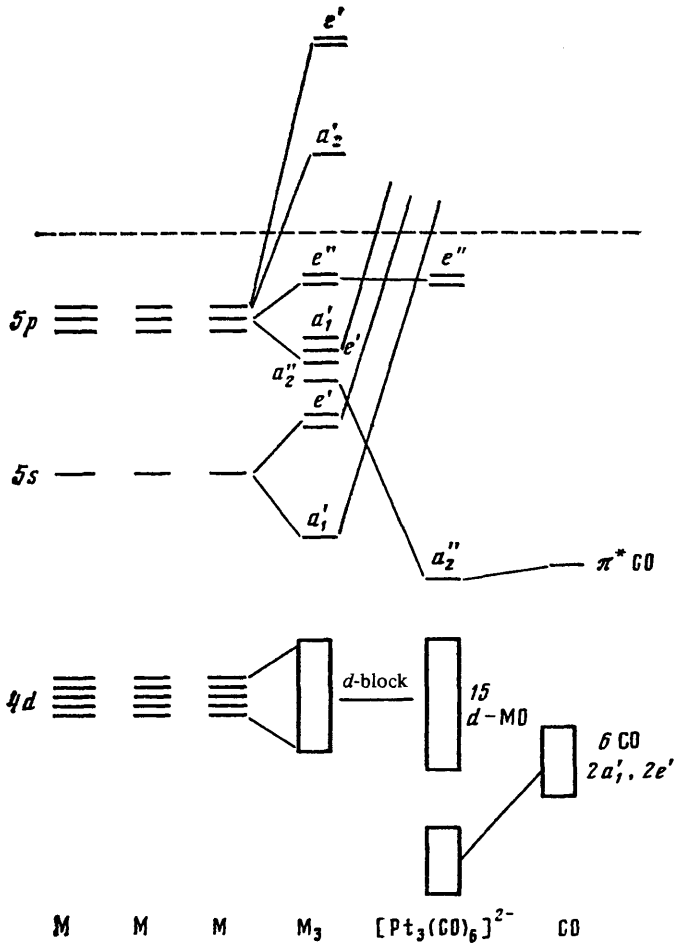

Figure 10 A qualitative scheme for the interaction of the AO of metals in the formation of a ligand-free M_3 triangle;[164] the changes occurring on formation of the anion $[Pt_3(CO)_6]^{2-}$ are shown on the right.

In the cluster compounds with 48 CVE all 24 CVMO are occupied, while in compounds of other types the situation is more complex. When the metallic triangle of the framework interacts with ligands (for example, with CO ligands) the cluster MO made up of the *s* and *p* AO undergo the greatest changes. Although the relative order in which the individual *d* orbitals are arranged changes somewhat on interaction with ligands (Figs.10 and 11), these changes are comparatively small, probably owing to the relatively small integrals, i.e. $[S] \leq 0.1$, for the overlap of the *d* orbitals of the metal with the orbitals of ligands such as the CO group.[165] Calculations have shown that the entire set of 27 MO of triangular clusters can be divided into four main groups, boundaries between which are approximate and vary as a function of the nature of the metals and the ligands. The molecular orbitals with the lowest energies are used mainly for bonding with the ligands because the combination of three *s* and nine *p* orbitals has the symmetry and directional properties suitable for bonding with ligands. The remaining five *d* orbitals form a set of MO having similar energies (the *d* block), through which the direct metal–metal interaction takes place. Next follow the so-called frontier orbitals, both HOMO and LUMO. Finally the antibonding orbitals with the highest energy belong to the fourth group.

This subdivision can be seen clearly in relation to the MO obtained as a result of EHM calculations for the $Ru_3(CO)_{12}$ molecule (Fig.11).[165] Examination of the character of the frontier orbitals of greatest importance for chemistry led to the conclusion that 48-electron metallocycles of the type of $M_3(CO)_{12}$ with D_{3h} symmetry are "inorganic" analogues of cyclopropane;[106] this analogy does not apply solely to the topological correspondence of the structures and the nature of the frontier orbitals; it is more profound and embraces also chemical behaviour: the similarity of $M_3(CO)_{12}$ to cyclopropane in the ring opening and closure reactions has been established in relation to $Os_3(CO)_{12}$.[167]

The $M_3(CO)_{12}$ clusters can be constructed by combining three octahedral $M(CO)_4$ fragments; the frontier orbitals of such fragments are illustrated in Fig.12. Two hybrid frontier orbitals of the a_1 and b_2 types, analogous to the σ and *p* orbitals of methylene, are located over a low-lying weakly split level mostly corresponding to the t_{2g} level in octahedral complexes. The $Fe(CO)_4$ and CH_2 fragments are isolobal and each has at least one pair of electrons in the two frontier orbitals indicated. The formation of the frontier orbitals of $Fe_3(CO)_{12}$ by combining the orbitals of the three $Fe(CO)_4$ groups, analogous to the formation of the orbitals of cyclopropane from those of the three CH_2 groups, is illustrated in Fig.12.[106] Evidently the orbitals of the t_{2g} level interact weakly with one another, forming the orbitals of the cluster *d* block, while the a_1 and b_2 orbitals give rise to a set of MO of the Walsh type. The difference from cyclopropane consists in the fact that both in the initial $Fe(CO)_4$ fragments and in the $Fe_3(CO)_{12}$ cluster the orbitals of the a_1 type have a higher energy than the b_2 orbitals, while in the cyclopropane the opposite situation obtains. It is believed[106] that this order in the arrangement of the orbitals is confirmed by the results of the investigation of the electronic and photoelectron spectra of $M_3(CO)_{12}$, where M = Ru or Os,[59] indicating the non-degenerate character of the HOMO in these compounds.

An analogous set of frontier orbitals of another 48-electron metallocycle, namely $Co_3(CO)_9(\mu_3\text{-}CH)$, is obtained by combining the orbitals of the $Co_3(CO)_9$ and CH fragments (Fig.4). It can be assumed that in other 48-electron triangular cluster compounds the qualitative scheme for the arrangement of the MO and their occupation by electrons is the same as for the molecules examined above. Information about the

character of the LUMO in such systems has been obtained in studies of the EPR spectra of certain 49-electron compounds presented in Table 5. Unfortunately there are as yet no experimental data which would permit the estimation of the energy gap between the HOMO and LUMO. The entry of a second electron into the LUMO results in the rupture of one metal–metal bond in the triangle.

Thus the scheme for the electronic structure of 48-electron triangular clusters put forward in a number of studies explains satisfactorily the existing experimental data. From this scheme, it follows without a doubt that triangular cluster compounds in which the number of CVE is greater than 48 should have greatly "loosened" metal–metal bonds up to an appreciable weakening of the direct interaction between the metal atoms. The stability of such cluster compounds is determined mainly by the μ_3-ligands which span the metallic triangle. For example, there are 53 CVE in the $Ni_3(\mu_3\text{-}S)_2.(Cp)_3$ cluster; the Ni–Ni bond length in this cluster is 2.80 Å,[159] which is greater by 0.4 Å than in the compound $Ni_3(\mu_3\text{-}CO)_2(Cp_3)$ with an analogous structure,[57] which has 4 CVE less [R(Ni–Ni) = 2.39 Å]; the five excess electrons in the $Ni_3(\mu_3\text{-}S)_3(Cp)_3$ cluster occupy three antibonding orbitals, while the weak Ni...Ni bonding is determined mainly by the exchange interaction involving the single unpaired electron ($\mu_{eff} = 1.7\ \mu_B$).

The data examined in Section II show that three-membered metallocycles with 48 CVE are characteristic of metals with the d^8 configuration or one close to it. However, clusters with fewer CVE are just as common; they can be divided into two groups—three-membered metallocycles made up of the atoms of the metal at the beginning of the transition series and triangles made up of the atoms of platinum group metals. It is striking that sometimes formally the same number of CVE can be attained by a different pathway—by introducing platinum metals or Group VI metals (Cr, Mo, and W). However, the electronic structure of the metallic framework in such cluster compounds is different. In platinum metallocycles the Pt–Pt distances (2.65–2.79 Å) differ little from the metal–metal distance in metallic platinum (2.77 Å), while in triangles made up of Group VI metal atoms the metal–metal distances are significantly shortened.

It might have been supposed that multiple metal–metal bonds are formed in triangles made up of atoms of metals having the d^6 or lower configuration, particularly since the existence of multiple bonds in dinuclear compounds of the same metals is a well established fact. For example, the results of quantum-calculations for model Cr, Mo, Ru, and Rh dimers, in which the metal atoms are linked by four identical planar bridges (O_2CH) located in pairs in mutually perpendicular planes and shielding fairly densely the space between the metal atoms, have been described;[3] the real molecules can each have in addition two two-electron axial ligands L. In the rhodium dimer each metal atom has a filled electron shell (taking into account the two electrons from the axial ligands L). The metal–metal bond orders are unity. In the isostructural ruthenium dimers there are two fewer electrons, while in the chromium and molybdenum dimers there are six fewer electrons. The rigid configuration of the dimers makes it impossible to attach additional ligands and make good from outside this electron deficit. The 18-electron shell in each metal atom in these compounds is therefore produced as a result of the formation of metal–metal multiple bonds; the bond multiplicity is 2 in the ruthenium dimer and 4 in the chromium and molybdenum dimers. In terms of the chosen coordinate system,[3] in the rhodium dimer the HOMO with $2b_{1u}$ symmetry is at the same time the antibonding δ^* orbital in relation to the metal–metal δ-bond; when it is filled with electrons, the δ-bond is ruptured and, conversely, a decrease of the number of electrons in this orbital leads to the appearance of a δ-bond

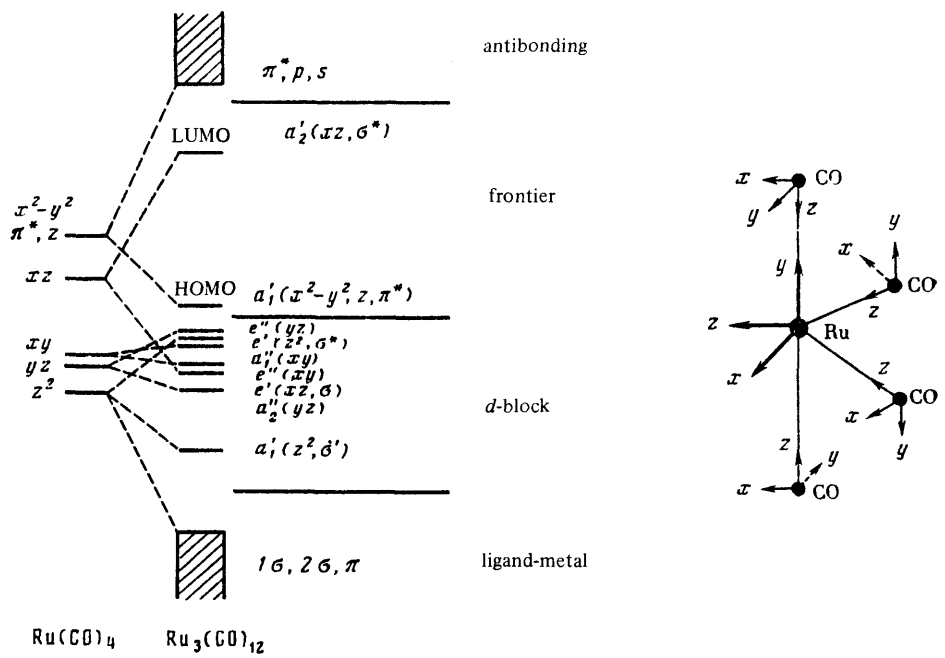

Figure 11. The formation of the molecular orbitals of $Ru_3(CO)_{12}$ from the MO of the $Ru(CO)_4$ fragment; HOMO = xz and LUMO = π^*, z for the $Ru(CO)_4$ fragment; the coordinate system for the $Ru(CO)_4$ fragment is shown on the right.[165]

between the metal atoms on moving along the above series of dimers from right to left; the same considerations are applicable to the π orbital which follows the δ^* orbital (see Cotton and Walton[3], pp.366–382).

One cannot rule out the possibility of a similar approach to the consideration of the electronic structures of three-membered metallocycles. The decrease of the number of intrinsic *d* electrons in the metal atoms and the impossibility of making good this deficit by attaching ligands should result in the occurrence of additional interaction between the AO of the metals with formation of multiple bonds.

Among electron-deficient clusters, quantum-chemical calculations have been made mainly for the Re_3 metallocycle;[59] they agree well with the hypothesis that multiple bonds are present in this and similar compounds. For example, the results of EHM calculations for the $(Re_3Cl_{12})^{3-}$ ion led the authors[166] to the conclusion that the two-centre bonds between the rhenium atoms can be described as double bonds.

Thus there are grounds for the assumption that, for the majority of the compounds listed in Tables 6–8 subject to the condition that the normal geometry of the framework and of the ligand environment is conserved, a decrease of the number of CVE compared with 48 for metals to the left of the iron group in the Periodic System can involve the formation of metal–metal multiple bonds in the metallocycle.

The normal multiplicity of each metal–metal bond (q) in a three-membered metallocycle can be calculated from the formula

$$q = \frac{54 - n}{6}$$

where 54 is the maximum number of electrons when all the 27 MO of the trinuclear cluster are occupied, n the number of CVE in the given three-membered metallocycle, and 6 the number of electrons capable of being accommodated in the three residual vacant CVMO in clusters with a filled shell having 48 CVE and a metal–metal bond multiplicity of unity.

Thus in the presence of 46 CVE the multiplicity of each metal–metal bond is 1 + 1/3, when all the bonds are equalised, or two M–M bonds have a multiplicity of unity and a third a multiplicity of two. This situation obtains, for example, in the 46-electron cluster $Os_3(\mu\text{-}H)_2(CO)_{10}$, where the bond between the two Os atoms spanned by two μ-H bridges has a multiplicity of 2, while the other two bonds have a multiplicity of unity; see also Cotton.[162]

From general considerations, it is understandable that the decrease of the bond lengths with increasing multiplity of the metal–metal bond in trinuclear metallocycles should be relatively smaller than in dimers. The difference between

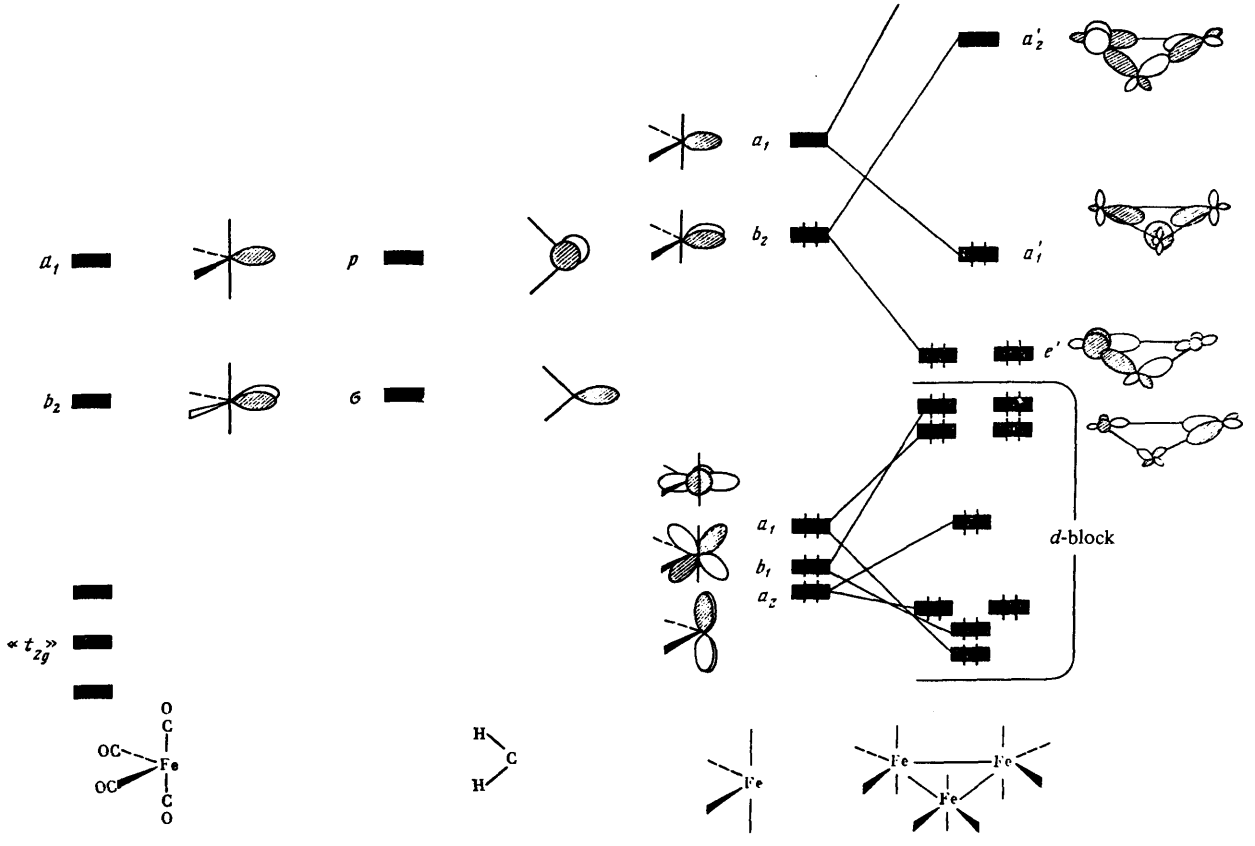

Figure 12. The group orbitals of the $Fe(CO)_4$ and CH_2 fragments; the formation of the MO of the $Fe_3(CO)_{12}$ molecule (idealised geometry with D_{3h} symmetry) from the orbitals of the $Fe(CO)_4$ fragments is shown on the right-hand side.[106]

the lengths of bonds of different multiplicity probably becomes increasingly less appreciable with increasing nuclearity of the clusters.

It follows from the calculated and experimental results presented above that triangular clusters based on platinum and palladium with a deficiency of electrons are as a rule coordination unsaturated and it would appear that they could combine with one or two more ligands in order to build up their electron shell to a stable state, but this does not occur in reality. In other words a triangle of Pt or Pd atoms can combine with a smaller number of ligands than the triangles made up of atoms of the other metals examined above. Furthermore, in heterometallic triangles each Pt or Pd atom reduces the total number of two-electron ligands by unity.

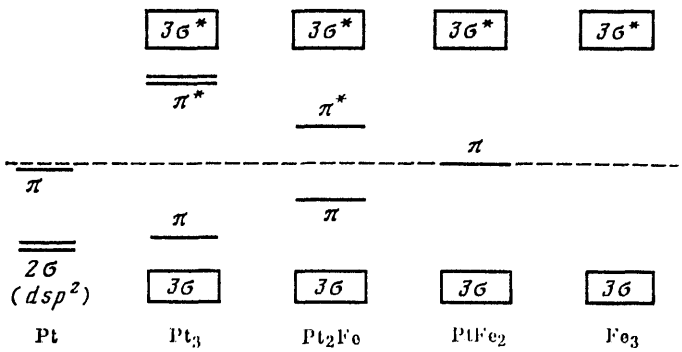

Figure 13. A qualitative scheme for the π-interactions in three-membered metallocycles with participation of platinum.[94]

It has come to be assumed that the energy of one of the *p* orbitals of the Pt or Pd atoms is unduly high and the orbital cannot participate in the formation of a bond with the ligand. Three such orbitals, extended along an axis perpendicular to the plane of the M_3 ring form as a rule in such cases the set of three MO illustrated schematically in Fig.13.[94] It is believed that these orbitals should have energies within the energy gap between the HOMO and LUMO for clusters with a filled electron shell. The changes occurring in the region of the frontier orbitals in the regular transition from Fe_3 to Pt_3 clusters are shown schematically in Fig.13. As a result of this interaction, one of the π MO becomes weakly bonding and two others become weakly antibonding.

This qualitative scheme agrees in the main with the results of an EHM calculation for the planar dianion $[Pt_3(CO)_6]^{2-}$, which are presented in Fig.10. Evidently all the 15 MO of the *d* block are occupied and the two excess electrons are in the a_2'' orbital, which has predominantly the π^*_{CO} character. The unoccupied non-bonding orbitals of the e'' set are in essence the almost unchanged *p* orbitals of the M_3 framework; calculations have shown that, in compounds with 42 CVE, all the orbitals having the *p* character ($a_2'' + e''$) are unoccupied.[164]

Thus an additional interaction of the π type also occurs in triangles based on platinum and its analogues, however, it does not involve the *d* orbitals, as in the previous case, but the MO made up of orbitals of the *p* type. However, in connection with the weakly bonding character of these MO, an appreciable decrease of the metal–metal distances does not as a rule occur.

The ability of platinum triangles to be coordinated to one another with formation of prismatic structures of different lengths, which are characterised by a weak interaction between the rings (the Pt–Pt bond length is greater than 3 Å) has been explained by the presence of orbitals of this type.

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Thus comparison of the structures and numbers of CVE in a wide range of three-membered metallocycles permits the conclusion that the magic number of 48 CVE for triangular clusters means merely that in the presence of a large number of CVE, the triangular structure of the framework with short metal–metal bonds cannot be retained; on the other hand, experience has shown that, when the number of CVE is reduced, the extent by which it differs from the magic number for triangular clusters can vary within fairly broad limits.

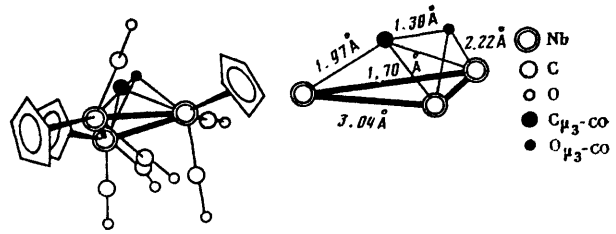

Figure 14. The structure of the $Nb_3(\mu_3\text{-CO})(CO)_6(Cp)_3$ cluster.[168]

On the other hand, one should note that in the chemistry of cluster compounds there is apparently no rigid specification whatsoever of the numbers of CVE for particular types of metals and ligands. It was noted above that, as one moves to the left along the Periodic System and the number of electrons in the valence shell of the metal atom falls, the number of CVE in the corresponding triangular compound differs to an increasing extent from the magic number. However, the $Cp_3Nb_3(CO)_7$ triangular niobium cluster with 48 CVE has been obtained, its structure being shown in Fig.14.[168] For this compound to have 48 CVE, the seventh CO group must supply six electrons for the formation of bonds with the metal atoms and for this to happen it must be located parallel to the plane of the Nb_3 ring. Fig.14 shows that this condition is fulfilled with adequate precision. The stretching vibration frequency of the seventh CO group is then displaced so much (to 1330 cm^{-1}) that in this case one can apparently envisage two ligands (C and O) weakly interacting with one another on the surface of the metallocycle. Consequently, if the ligand environment, occupying almost the same volume around the M_3 ring, can supply a greater number of electrons, a configuration with a filled electron shell obtains even for an element such as niobium, which has only five *d* electrons.

The same picture has been observed for the cluster compounds of metals having a filled *d* shell. Although triangular Pd and Pt clusters having 48 CVE have not so far been

obtained, one may quote an example from the chemistry of tetrahedral clusters. The magic number for the tetrahedron is 60 CVE; the majority of tetrahedral Pd and Pt compounds have, like the corresponding triangles, a significantly smaller number of CVE, but the $Pd_4(\mu\text{-}CO)_6(PBu_3)_4$ cluster with a tetrahedral structure of the framework has 60 CVE.[169]

In the formation of each given cluster compound there probably exist limited possibilities for the selection of ligands; a tendency is observed towards the construction of the most compact molecule with a preferential filling of the space around the metallic framework. Since the metallic framework itself is fairly stable, for example, in the form of ultradisperse metallic particles,[52] the electronic requirements which must be met by the ligand in the formation of a cluster on its basis are not rigorous, permitting deviations from the magic numbers. The number of examples in which the number of CVE differs from the magic number will apparently increase in the future as experimental data accumulate, particularly for cluster compounds with a high nuclearity.

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The Structure of Cluster Compounds of Transition Metals and the Limits of Applicability of the Electron Counting Rules for Polyhedral Molecules

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The current theoretical ideas concerning the electronic structure of clusters and electron counting schemes for them derivable from molecular orbital analysis, whereby one can determine magic numbers of valence and skeletal electrons corresponding to energetically favourable characteristic geometrical configurations of cluster polyhedra, are examined. Among the multiplicity of polynuclear compounds, the class of superaromatic clusters obeying Wade's rule (the $2n + 2$ rule) has been isolated. The structures of transition metal clusters M_n with $n = 3-38$, including small, trigonal-bipyramidal, and octahedral clusters, polyhedra of medium dimensions, and large clusters, are considered and the applicability of the existing schemes to the determination of magic numbers for each of these groups of compounds is discussed.
The bibliography includes 150 references.

CONTENTS

I. Introduction 323
II. Qualitative theoretical schemes for the electronic structures of cluster compounds of transition metals 323
III. The structure of transition metal clusters 331

I. INTRODUCTION

The present state of transition metal cluster chemistry can be best defined as the stage involving a vigorous search for regularities in order to arrange systematically and explain the entire extensive and varied experimental data. The unusual structure of the polyhedra made up to metal atoms in cluster molecules, the existence in the latter of a new type of bonding not observed in classical chemistry, and the increasing prospects for the use of clusters in catalysis—all these factors have been responsible for the continued rapid expansion of synthetic and structural research in this field.[1-9] Questions concerning the electronic structure of transition metal clusters[10] and related polyhedral molecules[11] have been frequently discussed also in Soviet chemical literature.

At the same time current theoretical ideas in cluster compound chemistry do not yet enable experimenters to predict the structures and reactivities of most of the newly obtained clusters and to estimate even in broad outline the most probable composition of the products of the reactions involving polynuclear molecules. The first fundamental studies designed to find correlations between the stoichiometry of cluster compounds and their geometrical and electronic structures were published more than ten years ago,[2,3] but the task of constructing a non-contradictory theory of the chemical bonds in clusters is still (despite the large number of studies carried out in recent years) far from complete and each of the existing theoretical concepts can account for the experimental facts relating to only a comparatively narrow class of compounds and is usually not concerned with the discussion of the numerous exceptions to a particular suggested rule. We therefore thought it timely to write this review, with the aim of introducing the reader to the range of theoretical problems in cluster chemistry, to give a critical survey of the existing models of the electronic structure of cluster compounds, and to define the limits of applicability of these models on the basis of experimental data.

The first part of the review deals with the theoretical schemes for the electronic structures of transition metal clusters current in the present-day chemical literature, while in the second predictions based on these theoretical schemes are compared with existing structural data. Among theoretical studies, those of a generalising character as well as calculations of the electronic structures of specific clusters, which enabled their authors to reach conclusions applicable to a certain group of polynuclear compounds, were considered in the first place. According to the estimates in Raithby's review,[7] the number of structural studies already exceeded 400 by 1980 and has continued to increase rapidly, which makes an exhaustive consideration of ali the available X-ray diffraction data cumbersome and obsolescent. We have therefore carried out a compilation of structural clusters only to the extent that this has been necessary to illustrate the adequacy or inadequacy of theoretical models for such clusters and the compilation embraces mainly recent studies.

II. QUALITATIVE THEORETICAL SCHEMES FOR THE ELECTRONIC STRUCTURES OF CLUSTER COMPOUNDS OF TRANSITION METALS

The primary task in the chemistry of cluster compounds has been from its inception the explanation of the clear preference for the formation of specific metallopolyhedra containing so-called "magic numbers" of valence electrons. Subsequently, we shall use the term "magic numbers" of electrons in the clusters (the valence electrons) determined from the stoichiometry of the latter as well as electrons assigned to the molecular orbital subsystem characteristic of the clusters—the so-called "skeletal" electrons (see below). These magic numbers have proved in many instances to be a stable characteristic of clusters differing in composition but having similar structures, i.e. a characteristic of a given classified metallopolyhedron. Thus in the majority of trinuclear clusters a closed triangular fragment M_3 (where M is a transition metal) contains 48 valence electrons, a 60-electron configuration is typical for tetranuclear tetrahedral clusters, an 86-electron configuration is typical for hexanuclear octahedral clusters, etc. The total number of valence electrons is then determined in accordance with the scheme usual in organometallic and coordination chemistry: the number of electrons provided by all the ligands in accordance with the usual rules

and in the case of charged clusters also the charge with the sign reversed are added to the total number of electrons in the valence shells of the atoms forming the cluster.†

The molecular orbital (MO) schemes widely employed in the chemistry of organometallic and complex compounds have been used since the beginning of the 1960's to interpret the electronic structure of clusters and to justify their magic numbers.[12,13] These schemes, to be referred to in the subsequent exposition as qualitative (bearing in mind their descriptive character), have remained hitherto the principal element of theoretical analysis in the chemistry of clusters—frequently owing to the difficulty of rigorous quantum-chemical calculations but in the first place because of the possibility of discovering in the simple model the fundamental properties of the molecule. However, the principle underlying the construction of the MO scheme is different in different approaches.

In its classical form, the diagram of one-electron levels of the cluster is constructed from the atomic orbitals (AO) of its constituent metal atoms and the frontier orbitals of the ligands which are used to make up linear combinations transformed in accordance with the irreducible representations of the symmetry point group of the molecule. The relative positions of the energy levels are then determined on the basis of particular qualitative (in reality rather intuitive) considerations. This approach, which was common in the chemical literature of the 1960's and is still sometimes used, appears, however, to be rather useless for the mononuclear transition metal complexes; in reality the number of MO is too large to regard any one of their dispositions as uniquely correct without resorting to additional data. It is therefore not surprising that the molecular-orbital models of the electronic structure of polynuclear complexes almost always involve an appeal to the results of calculations mostly carried out by the extended Hückel method (EHM). The models, with the aid of which certain important generalisations have been achieved, will be examined below in order of increasing complexity.

1. Clusters with Localised Bonds and the Effective Atomic Number (EAN) Rule

Soon after the start of systematic studies on clusters with carbonyl and olefin ligands, it was established that the magic numbers for some of them can be readily obtained by extending Sidgwick's rule [the 18-electron shell or the effective atomic number (EAN) rule] to some of them. This extension is based on the important postulate of the localised, i.e. two-electron two-centre, character of the metal–metal bonds in the polynuclear derivatives considered. Clusters satisfying this postulate are illustrated in Fig.1, which also presents the corresponding numbers of valence electrons N_{val}.

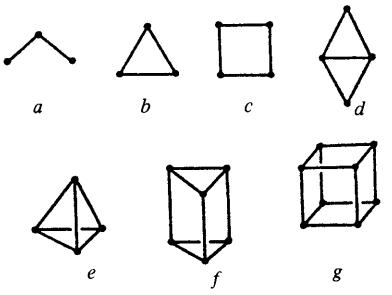

Figure 1. Clusters satisfying the EAN rule and the numbers of valence electrons N_{val} in their metallopolyhedra: *a*) $Os_3(CO)_{10}(\mu_3\text{-}Br)_2$,[15] 50ē; *b*) $Fe_3(CO)_{12}$,[14] 48ē; *c*) $Pt_4(OAc)_8$,[16] 64ē; *d*) $[Re_4(CO)_{16}]^{2-}$,[17] 62ē; *e*) $M_4(CO)_{12}$ (M = Co or Rh),[18] $Cp_3Cr_3Co(CO)(\mu_3\text{-}S)_4$,[19] 60ē; *f*) $[Rh_6C(CO)_{15}]^{2-}$,[20] 90ē; *g*) $Ni_8(CO)_8(PPh)_6$,[21] 120ē (OAc = $OOCCH_3$, Cp = $\eta^5\text{-}C_5H_5$).

The approach based on the EAN rule in essence reduces the electronic structure of clusters to the structure of their simplest analogues—organic or inorganic compounds (tetrahedrane, cubane, prismane, etc.—see Fig.1).# This analogy has been justified also in quantum-chemical calculations: many workers[3,22–25] have established that in model "naked" clusters M_n with M–M distances amounting to 2.5–3.0 Å and characteristic of real transition metal clusters, the splitting of the AO of the *d* block as a result of the formation of metal–metal bonds is insignificant compared with the splitting of the *s* and *p* AO of the valence shell. As a consequence of this, the *s* and *p* AO of the metal atoms make a dominant contribution to the bonding orbitals of the cluster and also to its high antibonding molecular orbitals, the filling of which with electrons leads to the breakdown of the M_n polyhedron. Thus in the stable M_4 tetrahedron with six localised metal–metal bonds the six corresponding antibonding MO should remain vacant, which in fact accounts for the magic numbers for this cluster: $N_{val} = 60$ ($18 \times 4 - 2 \times 6 = 60$).

The EAN rule makes it possible to isolate from the multiplicity of polynuclear complexes and clusters polyhedra related to skeletal compounds in organic chemistry. It is important to note that not more than three edges converge in the vertices in all the clusters illustrated in Fig.1. This geometrical characteristic of clusters with localised bonds probably has a profound topological significance.

†Another scheme for counting electrons in which one begins with a formal ionic structure for the complex and a d^n configuration usually attributed to the residual valence electrons in the transition metal, is current in inorganic chemistry. Clearly there is a rigorous relation between the total number of electrons in the cluster in such an "inorganic" scheme and the total number of valence electrons of the cluster determined in accordance with the "organometallic" scheme, but the numbers are different. This self-evident factor is sometimes forgotten in the consideration of cluster systems, the number of *d* electrons of the model ion (d^n) being used incorrectly in Wade's scheme (see Section II below). The "inorganic" scheme is usually employed in studies of the structure of clusters with halide ligands; in the chemistry of carbonyl clusters and their derivatives, the total number of all the valence electrons is usually considered. To avoid confusion, we shall use in the subsequent exposition only the "organometallic" approach (with the exceptions examined in subsections 1 and 3 of Section II).

#In contrast to skeletal organic compounds, the atom of a light element (H or C) can be incorporated in trigonal-prismatic metal clusters {as in the 90-electron cluster $[Rh_6C(CO)_{15}]^{2-}$ (Fig.1)}. In such derivatives the inserted atom supplies to the polyhedron all the electrons of its valence shell to be used for bonding.

2. Clusters with Many-Centre Bonds and the 2*n* + 2 Rule

Despite its simplicity and effectiveness, the EAN rule is unfortunately not entirely general and embraces only one class of polyhedra with localised metal–metal bonds. On the other hand, structural and chemical studies have made it possible to establish umambiguously that the chemical bond in the majority of cluster compounds is delocalised (many-centre) and does not reduce to the sum of two-centre two-electron interactions.[2] Thus, by placing along each edge of the polyhedron a two-centre two-electron bond even in hexanuclear octahedral clusters, we obtain 12 antibonding MO, the condition for the latter being unoccupied requiring the presence of 84 valence electrons in the cluster ($18 \times 6 - 2 \times 12$), while a magic number of 86$\bar{e}$ is characteristic of the vast majority of such clusters with carbonyl and olefin ligands. On the other hand, another hexanuclear cluster (a trigonal prism) does indeed have $N_{val} = 90$ ($18 \times 6 - 2 \times 9$) in conformity with EAN rules. Thus the transition from a polyhedron with third-order vertices, i.e. vertices joined to three other vertices (for example a trigonal prism), to a polyhedron with fourth-order vertices (for example, an octahedron) alters radically the character of the chemical bond in the cluster.

A magic number of 86$\bar{e}$ was noted in the 1960's virtually in each structural study on octahedral transition metal clusters (see, for example, Cotton and Haas[12] and Corey et al[13]), usually illustrated by a qualitative MO scheme in which numerous electronic levels, both degenerate and non-degenerate, are considered. A logical explanation and a scheme permitting the calculation of the magic numbers for clusters of a specific type with an arbitrary number of vertices were first proposed by Wade.[2,26] In his studies, initially devoted to the electronic structure of polyhedral boron hydrides and carbaboranes,[26] these compounds were subsequently proposed as a correct model for the description of the bonding in metal clusters with electron delocalisation—just as the skeletal organic molecules indicated above can serve as models for clusters satisfying the EAN rule.

Wade's scheme is based on the extremely important hypothesis that the electron system of the polyhedral molecule (carbaborane or metal cluster) is divided into two independent subsystems: the exopolyhedral and skeletal subsystems, which greatly resembles the familiar differentiation of the σ- and π-electron systems in planar aromatic molecules. Such subdivision was first established as a result of quantum-chemical calculations for the simplest polyhedral boron hydrides.[27] The calculations showed that polyhedral molecules with *n* vertices and triangular faces (*closo-n*-gons or deltahedra) contain *n* + 1 bonding MO made up predominantly of the AO of the atoms in the polyhedral skeleton distributed in the scheme in the "upper" (with a higher energy) part of the block of the bonding MO and separated from the antibonding MO by a considerable energy gap.

After comparing the results of structural and computational studies, Wade proposed the "2*n* + 2" rule,[26] according to which any *closo-n*-gon contains *n* + 1 skeletal bonding MO in which 2*n* + 2 skeletal electrons can be accommodated after the attainment of the closed configuration. The presence of a non-triangular ("open") face leads to an increase of the number of skeletal bonding MO by one and hence to the existence of 2*n* + 4 skeletal electrons in the *nido-n*-gon with one open face, of 2*n* + 6 skeletal electrons in the *arachno-n*-gon with two open faces, of 2*n* + 8 skeletal electrons in the *hypho-n*-gon with three open faces, etc. The appearance of a "cap", i.e. of an additional vertex located above the triangular face, in the polyhedron, which is frequently observed in metal clusters, does not increase the number of skeletal MO of the main polyhedron and the number of skeletal electrons supplied by this vertex is calculated in the same way as for the other vertices in metal clusters. The additional atom inserted into the polyhedral cavity also does not alter the number of skeletal MO and supplies its valence electrons to the skeletal bonding system in the cluster.

The scheme which Wade proposed[26] for counting electrons in a cluster employs the additional postulate of the involvement of three AO of the atom occupying the vertex of the polyhedron and the formation of skeletal MO. In the exopolyhedral system of orbitals of this atom (which is responsible for bonding with the ligands and which accommodates the unshared electron pairs) there remain respectively one AO in the case of a non-transition element and six AO in the case of a transition element. Thus the number of electrons introduced into the polyhedron for "skeletal" bonding by the mononuclear fragment located at its vertex is $x + l - 2$ for an atom of a non-transition element at the vertex of the polyhedron and $x + l - 12$ in the case of a transition metal atom, where x is the number of valence electrons of the given atom and l the number of electrons supplied by the ligands bound to the given atom.

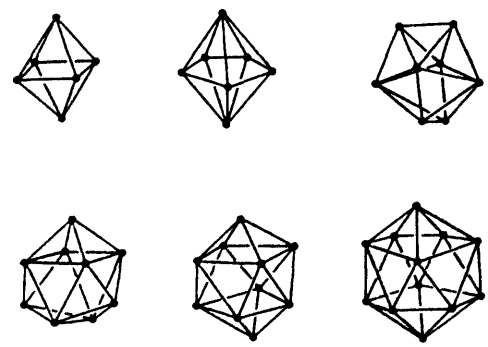

Figure 2. Types of metallopolyhedra in clusters with delocalisation of skeletal electrons.

According to this scheme, the $(OC)_3Fe$ and CpCo fragments each supply two electrons to the skeletal bonding system of the polyhedron, while the $(OC)_3Co$ fragments supply three electrons—in the former case analogously to the BH fragment and in the latter analogously to the CH fragment. The total number of skeletal electrons in an *n*-nuclear homoatomic cluster made up of transition metal atoms is then $n(x + l - 12) - q$, where q is the charge of the cluster, and is related to the number of vertices and open faces of the polyhedron by Wade's rule. The number of skeletal electrons can be found from the number of valence electrons and conversely (in the case of clusters made up of transition metal atoms $N_{val} = N_{sk} + 12n$, where n is the number of transition metal atoms). Thus octahedral clusters with 86 valence electrons contain 14 skeletal electrons, i.e. $86-12 \times 6$, in conformity with Wade's rule (*closo*-6-gon, $2n + 2 = 2 \times 6 + 2$). The magic number 86$\bar{e}$ for an octahedral cluster has thus been accounted for.

The 2*n* + 2 rule and the associated scheme for the counting of electrons, nowadays frequently referred to as the theory of skeletal electron pairs, has made a significant contribution to the theoretical ideas in the chemistry of clusters. The similarity of the structures of metal clusters and polyhedral

molecules such as those of boranes, carbaboranes, metalloboranes, and metallocarbaboranes, π-complexes, and nonclassical cations has been established on their basis.[2,3] With the aid of the $2n + 2$ rule, chemists have been able to predict the structure of a cluster on the basis of its stoichiometric composition.

The relation between the $2n + 2$ and EAN rules can be readily accounted for in terms of the postulate, adopted by Wade, that three AO of the atom at the vertex are involved in polyhedral skeletal bonding. Conditions for the formation of localised bonds are indeed fulfilled in clusters where all the vertices have an order $n \leq 3$ as a consequence of the overlap of the AO of neighbouring vertices in pairs. An increase of the order of the vertices in the polyhedron leads to a delocalised skeletal bonding system. Examples of the polyhedra encountered in the structures of carbaboranes and metal clusters are illustrated in Fig.2. We may note that the vertices of all these polyhedra have an order of four and above.

3. Lauher's CVMO Scheme and Other Approaches Based on EHM Calculations

The $2n + 2$ rule, which makes it possible to treat systematically the structures of a large number of clusters, has now become widely popular. The region of its applicability has proved, however, to be restricted to polyhedra of medium size, mainly made up of the atoms of Fe, Co, and their analogues with carbonyl ligands, some of which can be substituted by other "soft" ligands. Thus numerous clusters of other types remained outside the limits of Wade's scheme. Furthermore, Wade's rule itself is more in the nature of an empirical generalisation, leaving room for further development of the theory. The latest studies in the theoretical chemistry of clusters have accordingly developed in two directions: in ne of these the aim was to seek analogous schemes for the counting of electrons in other types of clusters and in the other the aim was to find a theoretical justification of the validity of the $2n + 2$ rule. In this subsection we shall consider the most widely used schemes developed in accordance with the first approach, while in the next subsection the results of the development of the second approach will be described.

The close relationship between clusters with localised and delocalised bonds which follows from the $2n + 2$ rule justifies the application to the latter of the model which made it possible previously to extend the EAN rule to clusters with localised bonds. According to this model, which we examined above, the highest antibonding MO of an isolated polyhedral M_n fragment are most important for the description of the electronic structure and for the determination of the magic numbers of the cluster; the filling of these MO by electrons is accompanied by the disruption of the cluster structure.[3,22] In contrast to clusters with localised bonds, such MO cannot be clearly represented by the sum of two-centre interactions; furthermore, for clusters of arbitrary type no *a priori* considerations are known at present which would permit a rigorous determination of the number of these MO. The significantly many-centre character of the bond in the clusters considered has given rise to a tendency to construct "canonical forms" with three-, four-, six-centre, etc. two-electron bonds and the resonance between such forms can evidently account for any number of valence electrons observed in reality. However, the predictive power of this scheme, described in Johnson and Benfield's review,[6] appears to us to be extremely insignificant, because procedures for a quantitative estimation of the contributions of the canonical forms considered to the overall resonance hybrid are not then defined (on the other hand, the main part of Johnson and Benfield's review,[6] devoted to studies of the configurations of ligands in carbonyl clusters, is extremely relevant and interesting). An attempt may be made to obviate the difficulties caused by the lack of rigorous theoretical principles for the prediction of the number of configurations of the antibonding MO of the cluster by constructing a MO diagram with the aid of quantum-chemical calculations. The first important results on these lines have been obtained by Mingos,[3] who confirmed by means of EHM calculations the validity of the selection of polyhedral B_6 molecules as a model of the Co_6 cluster. The calculated disposition of the highest antibonding MO made up of s and p AO in the B_6 and Co_6 clusters is indeed the same (Fig.3); the MO of the $3d$ type in the Co_6 cluster then constitute an extremely narrow band as a consequence of the less effective overlap of the corresponding AO.[3] The diagram obtained illustrates satisfactorily the applicability of the $2n + 2$ rule, derived for carbaboranes, to clusters of the metals in the centres of the transition series.

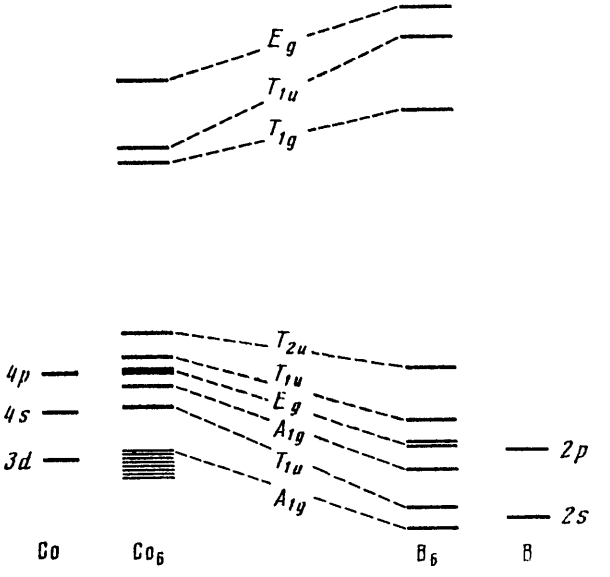

Figure 3. MO schemes for model Co_6 and B_6 clusters.[3]

The next step in the analysis of the MO with an isolated metal cluster was the scheme proposed by Lauher in a series of communications,[22,23] which is frequently referred to as the theory of valence MO of the cluster (CVMO) or of the valence electrons of the cluster. Lauher's scheme divides the MO of the cluster into low-lying CVMO and the antibonding MO (HLAO), designated here by AMO, separated from them by an energy gap. When ligands are coordinated to the cluster nucleus, the CVMO are modified as a consequence of their involvement in bonding while the AMO undergoes smaller changes (owing to the greater difference between their energies and those of the ligand orbitals) and remain unoccupied in the molecule of a real cluster. After differentiating the AMO on the molecular orbital diagram of the M_n cluster, calculated with the aid of EHM, the magic numbers of electrons

which can be accommodated in the CVMO of the given polyhedron when it is coordinated to the ligands are obtained. Specific calculations enable the author[23] to introduce the following semiquantitative criterion for the separation of the AMO from the CVMO: the antibonding MO of the cluster usually have higher energies than the unoccupied p AO of the metal atom.[23]

In contrast to Wade's scheme which operates with the intrapolyhedral (skeletal) electronic configuration, Lauher's scheme includes all the valence electrons of the cluster and is applicable in principle to metallopolyhedra having structures of any complexity, provided that the computational method employed in the scheme is sufficiently correct. Although a useful aspect of the qualitative scheme, namely the possibility of finding the magic number for a polyhedron of any structure without quantum-chemical calculations, is lost in this approach, it also makes it possible to determine the number of valence electrons in a specific M_n cluster with an arbitrary disposition of ligands in terms of a uniquely calculated MO scheme, although it does not provide a unique explanation of such numbers. On the other hand, in his first study,[22] Lauher reproduced, for example, the stable 170-electron configuration of the $[Rh_{13}(CO)_{24}H_3]^{2-}$ cluster with an Rh atom incorporated within the polyhedron, which cannot be interpreted in terms of other schemes, and carried out calculations for a series of M_n clusters with $n = 3 - 15$.

The total number of CVMO is expressed in Lauher's method as $6n + X$, where X is a quantity which assumes values from 3 to 13 depending on the geometry of the M_n polyhedron. The number of CVMO corresponding to one metal atom varies in conformity with this, converging slowly to 5.3, a value characteristic of an infinite metallic lattice, as the size of the cluster increases.

It appears that the CVMO scheme still suffers from the disadvantage that the prediction of the order in which the MO of the cluster are distributed on the basis of qualitative considerations is difficult and hence the results depend on the adequacy or inadequacy of the computational method employed. The extended Hückel method employed by Lauher (the simplest and therefore hitherto the only semiempirical quantum-chemical method used in calculations for systems such as polynuclear transition metal clusters) is by no means universal; its fundamental validity has been questioned even in calculations for mononuclear transition metal complexes.[28] An advantage of the EHM is that it takes into account the topology of the molecule by introducing into the matrix of the model Hamiltonian non-diagonal elements proportional to the overlap integrals. However, the question of the applicability of the given method to calculations for the molecules of organometallic and also cluster compounds is complex and requires further investigation.

In Lauher's study[22] the CVMO scheme reproduced correctly, in conformity with the predictions of the EAN or $2n + 2$ rule, the magic numbers for a series of common polyhedra (tetrahedron, trigonal prism, octahedron, cube, two-cap Archimedes antiprism, eicosahedron). However, results in conflict with the existing qualitative schemes and inconsistent with the magic numbers of the carbaborane analogues have been obtained for certain polyhedra (pentagonal pyramid, dodecahedron with trigonal faces, and square antiprism without caps). It is of interest to note that the real structure of transition metal clusters with such polyhedra of medium dimensions exhibits in reality deviations also from the predictions based on the $2n + 2$ rule, although this structure is not in fact fully consistent with Lauher's magic numbers either (see section II). For the octahedron with four caps, located in accordance with a tetrahedral motif, the predictions of the CVMO scheme ($N_{val} = 140$) have also not been confirmed: the corresponding osmium clusters of the type $[Os_{10}C(CO)_{24}]^{2-}$ contain 134 valence electrons in conformity with Wade's scheme.[29]§

The advantages and disadvantages of Lauher's approach are well illustrated by a study of Italian workers,[24] who quote the results of the calculation for more than 100 M_n metal clusters containing fragments of close-packed metal atoms. Calculation for eight Rh clusters of known structure, which served as models, made it possible (in some conflict with Lauher's data) to specify unambiguously the set of CVMO, corresponding to the real number of valence electrons, only for the three polyhedra of highest symmetry. In the remaining cases the numbers of valence electrons predicted did not agree with the real composition or a uniform distribution of levels was observed on the MO diagram, so that their separation into CVMO and AMO with respect to the energy of an isolated metal atom proved to be fairly arbitrary. In order to reduce the discrepancies between the calculated and observed numbers of electrons in planar trinuclear and tetranuclear clusters, it was necessary to choose as the AMO the orbitals whose energies were much higher than that of the unoccupied p level. Nevertheless, the authors[24] believe that the agreement between the calculated and experimental magic numbers is adequate for a qualitative consideration of the structure of transition metal clusters.

The numbers of CVMO determined by the above investigators[24] correspond to the formula $6n + X$ where X varies from 6 to 11. $X = 7$ was found for approximately half of the structures for which calculations had been made and $X = 8$ was found for one-quarter of the structures. Since the formal validity of the $2n + 2$ rule requires the existence of $2n - 1$ skeletal AMO and correspondingly $7n + 1$ CVMO, the authors[24] concluded that Wade's rule is inadequate for the class of systems which they investigated and proposed a $6n + X$ rule for an arbitrary n-atomic cluster, where in the majority of cases $X = 7$. This modification of Lauher's formula, which has been quoted recently in a number of communications, is in our view erroneous. The discrepancy between the number of CVMO of an n-vertex cluster and the

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§ In certain recently published communications (B.K.Teo, Inorg.Chem., 1984, **23**, 1251; B.K.Teo, G.Longoni, and F.R.K.Chung, Inorg.Chem., 1984, 23, 1258) the number of CVMO of an arbitrary M_n metal cluster has been determined without a preliminary calculation, solely on the basis of the EAN rule and Euler's theorem by means of the formula $8V + 2 - F + X$, where V is the number of vertices of the cluster, F the number of its faces, and X the number of "additional" electron pairs necessary to create a stable electronic configuration, in excess of the number required in accordance with the EAN rule for a cluster with localised M–M bonds. The introduction of the term X reflects the many-centre character of the bonding in the cluster; $X = 0$ in all polyhedra with third-order vertices. The values of X for stable clusters, including those made up of several polyhedra, are determined by a set of seven rules (supported by a qualitative examination of the MO). These rules make it possible to find the numbers of valence electrons N_{val} for a large number of clusters with carbonyl ligands which have been investigated. The discrepancies between the calculated and real values of N_{val} are then observed mainly for cluster compounds of the elements at the end of the transition series and for the majority of metal clusters. The empirical character of the rules, which frequently specify 2–3 magic numbers of valence electrons for the metallopolyhedra most frequently encountered (trigonal bipyramid, octahedron, the Archimedes antiprism, and a three-cap triangular prism) can apparently be regarded as one of the disadvantages of the proposed scheme.

"Wade" value of $7n + 1$ can in general indicate the inapplicability of the $2n + 2$ rule to the given polyhedron, because the rule is not universal. However, $X = 7$ is also not of general validity (see Table 2 in Lauher's paper[22]) and its frequent appearance in the results of calculations reflects mainly the fact that more than half of the metal clusters considered[24] are constructed on the basis of an octahedron or a tetragonal pyramid supplemented by different numbers of "caps" or other condensed polyhedra. In conformity with Wade's rule, the octahedron (*closo*-hexagon) or tetragonal pyramid (*nido*-pentagon) with an arbitrary number of caps should have seven skeletal electron pairs, which, when added together to the $6n$ exopolyhedral MO, yields precisely $6n + 7$ CVMO. In this case X is exactly equal to 7 (Wade's formula includes the number of vertices not centred on trigonal faces and not the total number of vertices of the polyhedron[2]).

The results of the above study[24] illustrate in a somewhat unexpected fashion the, on the whole, correct evaluation of the number of CVMO (and hence of the valence electrons) by EHM calculations for clusters where they can be calculated independently in accordance with the $2n + 2$ rule. However, for a series of clusters including the four-cap octahedron discussed above, numbers N_{val} inconsistent with the real values (see Section III) were obtained. The reasons for the adequacy of the computational scheme under consideration in the case of some polyhedra and its inadequacy for their closest analogues are not entirely clear and we believe that so far the results of EHM calculations should be treated with a certain amount of caution.

It might have been expected that the results of EHM calculations will become more applicable with increase of the number of atoms in the cluster and on transition to an infinite crystal lattice of the metal in the limit, because in this region of large clusters the qualitative chemical rules governing the electronic structure are so far unknown. However, in calculations for large M_n metal clusters with $n = 16$–22[22,24] it was shown that, with increase of the number of metal atoms, the MO system approaches ever more closely the continuous region where no subdivision into AMO and CVMO is observed.

The CVMO method has been criticised also from the standpoint of a physical approach in which clusters are treated within the framework of band theory. According to Wooley,[9] who describes the physical point of view on clusters, the extended Hückel method yields an unduly small d band width in polyatomic transition metal aggregates (~1 eV in Mingos's calculations and ~3eV according to the estimates of band theory) and generates a bonding pattern inconsistent with the limiting case of a metallic lattice in which the bonding electrons occupy the d band and the s and p electrons (the probability of finding such electrons in the inner shells of a neighbouring atom is not zero as a consequence of the diffuseness of the corresponding AO) are antibonding because of orthogonality factors. There is no doubt about the value of the approach to the structures of large metal clusters from the standpoint of the ideas of solid state physics (band theory), but one should note that in this field the interests of physicists and chemists sometimes do not coincide and studies of correlations of the "composition–structure–properties" type must nevertheless be based on theoretical considerations derived from fairly approximate chemical models.

As in other theoretical schemes in the chemistry of clusters, the CVMO method is not universal even when the EHM calculation is correct.[23] In particular, with its aid it is impossible to interpret the electronic structures of polynuclear platinum and gold compounds (although these admittedly cannot be described satisfactorily within the framework of other theoretical schemes either). Thus the octahedral cluster $\{Au_6[P(C_6H_4Me)_3]_6\}^{2+}$, containing 76 valence electrons, i.e. four skeletal electrons, does not fit any of the existing models.

The electronic structures of the numerous unusual platinum and gold clusters obtained in recent years have been interpreted by Mingos using the results of EHM calculations.[31–36] Gold clusters of medium dimensions ($n = 6$–13) have been considered taking into account two findings by the same investigator: (1) the slight overlap of the occupied d AO leading to the formation of a narrow d band of a weakly antibonding character and (2) the small contribution of high-energy unoccupied p AO of the Au atoms to the bonding in the cluster. As a zeroth approximation, Mingos adopted a simplified model taking into account only the interaction of the valence s AO of the Au atoms in the clusters; in essence, this model is analogous to that of the simple Hückel method, where account is taken only of the overlap between the orbitals of neighbouring atoms and the p AO of the π-system are replaced by the s AO of the atoms making up the polyhedron.[31] The simple orbital diagram obtained for this model agrees with the relative disposition of the s MO in a more complex schematic arrangement of levels calculated using valence s, p, and d AO as the basis. The s MO schemes for the octahedral and eicosahedral clusters are presented in Fig. 4.

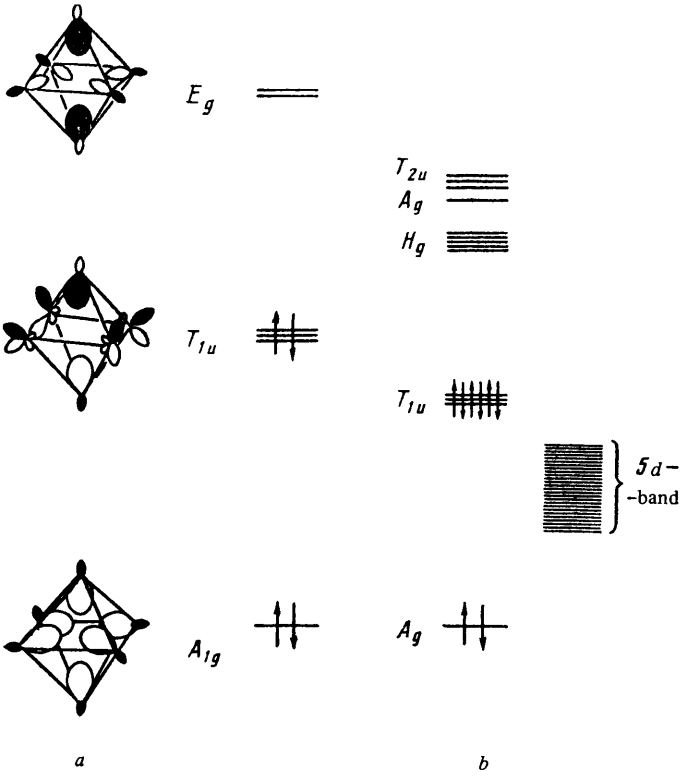


Figure 4. MO schemes for the Au_6 octahedral cluster (a) and the centred Au_{13} eicosahedral cluster (b).[31]

Mingos[31] demonstrated that the structures of the Au_n clusters based on a centred eicosahedron with the greatest contribution to the bonding by the interaction between the central and peripheral Au atoms are preferable. The coordination of n phosphine ligands at the vertices of such a

polyhedron results in the formation of n strongly bonding MO of the exopolyhedral type and the corresponding increase of the energy of the cluster s MO with retention of their relative positions.

The stable electronic configuration predicted by this calculation corresponds to the composition of the $[Au_{13}(PPh_3)_{12}]^{5+}$ cluster. This prediction was confirmed by the successful synthesis of the isoelectronic cluster $[Au_{13}L_{10}Cl_2]^{3+}$ with the *trans*-disposition of the Cl ligands in the eicosahedron.[32] Calculations for the octahedral $[Au_6L_6]^{2+}$ cluster predict an open electron shell [only two electrons are located in the triply degenerate T_{1u} MO (Fig. 4)], which subsequently led Evans and Mingos[33] to doubt the validity of the structural study of Bellon et al.[30] and the correctness of the composition established. The prediction of the stability of the octagonal dodecahedral Au_8C clusters with a carbide carbon atom at the centre of the polyhedron[31] has not so far been confirmed experimentally.

In the theoretical schemes examined above the cluster molecule is subdivided into the metallopolyhedron proper and its ligand environment and the electronic characteristics of the polyhedron, which depend little on the configuration of the ligands, are analysed. There exists also an alternative approach to the determination of the electronic structure of the clusters in which the MO scheme for the polyhedral molecule is constructed from the frontier orbitals of the mononuclear ML_k fragments. The idea, that the fragments of different nature whose frontier orbitals have similar energies and have the same nodal properties are stereochemically similar, occupies a major place in this approach. These considerations are to some extent already contained in Wade's classification of the mononuclear fragments of the cluster in terms of the number of electrons which they supply to the polyhedron, have been generalised in the familiar principle of isolobal correspondence,[36] and are widely used in interpreting the results of EHM calculations.[33–35] In this interpretation the analogy between the metal carbonyl clusters and polyhedral boranes and carbaboranes is justified by the isolobality of the $M(CO)_3$ and MCp fragments (where M is a transition metal) in relation to the BH and CH fragments. The development of schemes for the counting of electrons in polyhedral molecules outside the region of applicability of the EAN and $2n + 2$ rules, in this type of treatment is an expected result of the analysis of the correlation diagram of a cluster made up of mononuclear fragments such as $M(CO)_4$, ML_2, or ML, where L is a phosphine ligand, which are not isolobal with respect to the BH group. The last two fragments are encountered mainly in "non-Wade" Pt and Au clusters respectively; the magic numbers for small polyhedra with the number of vertices n between 3 and 6, which have been proposed on the basis of EHM results, were interpreted on the basis of the isolobal analogies of the given fragments.[33–35]

Nevertheless, the calculations have demonstrated the absence of adequate models for the AuL or PtL_2 fragments among the compounds of other elements. In the case of small Pt clusters, the electronic structure and the magic number derived from it proved to be different for different orientations of the ligands L relative to the Pt_n metallopolyhedra.[34] On the other hand, the energy of formation of Au clusters of different structure proved virtually identical in EHM calculations.[33] The isolobal analogy between the $Pt(PH_3)_2$ "corner" fragment and the $M(CO)_3$ "conical" fragment proved to be incomplete as a consequence of the energy splitting of the $hy(xz)$ hybrid orbital and the $p(y)$ atomic orbital, whose equivalents are degenerate in the case of $M(CO)_3$ (it is of interest to note that the frontier orbitals obtained in the studies quoted usually contain a significant contribution from d AO). The isolobal correspondence between the $AuPR_3$ fragment and the hydride ligand H has been postulated[33] for small Au clusters. It was deduced from structural data for the mixed clusters of the type $Os_3(CO)_{10}\cdot(AuPEt_3)_2$ [37] and $Ru_4(CO)_{12}(AuPR_3)_3H$, [38] where the $AuPR_3$ fragment as it were occupies the place of the μ-H ligand in the hydride derivatives, which have been synthesised recently. However, this analogy is incomplete and the authors stipulate the possibility in principle of the involvement in bonding also of the 6p AO of the Au atoms.[33]

On the whole, we believe that, with all its undoubted clarity and popularity, the analysis of the frontier orbitals of the fragments is in essence insufficiently effective for the prediction of the characteristics of the structure of polyhedral molecules which are at present not susceptible to description in terms of other schemes. The results of a number of studies[33–36] represent essentially the expression of experimental structural data in terms of frontier MO schemes and their explanation on the basis of a more detailed specification of the postulates which had already been put forward in earlier studies[31] and which involves certain controversial claims—the existence of two instead of three metal–metal bonds in 44-electron trinuclear Pt complexes[35] in the presence of 54 instead of 58 valence electrons in the $Au_4(\mu\text{-}I)_2(PR_3)_4$ tetrahedral cluster.[33] There is no doubt that consideration of a specific type of MO of the clusters gives rise to extensive possibilities for the interpretation of experimental data but the value of the theoretical scheme is largely determined by its predictive power. We believe that in this sense the principle of isolobal correspondence, which is extremely useful for the systematic treatment of a large number of molecular structures, may in many instances prove to be relatively inapplicable to the real structural-chemical problem.

4. The Topological Interpretation of the Electronic Structure of Cluster Systems

The ideas borrowed from topology and the graph theory have nowadays penetrated structural and quantum chemistry to an increasing extent. The development of studies on cluster molecules and the wide variety and unusual nature of the polyhedra present in them have led to a kind of fascination with the topological terminology, the employment of which in most of the studies published hitherto makes the interpretation of the results more novel than fruitful. Advances in theoretical chemistry and in the first place the study of the MO of planar aromatic systems by the graph theory method[39] have shown, however, that the application of the procedures of this, one of the most modern and abstract fields of mathematics, to chemical problems can be extremely useful and the possibilities for the introduction of topological ideas into the chemistry of cluster molecules are apparently much wider than the mere determination of the number of edges from the number of faces (or conversely) in an n-vertex cluster in terms of Euler's scheme. Topological ideas have been used to some extent in studies carried out in recent years whose aim was a theoretical justification of the $2n + 2$ rule.[40,41]

The book of King and Rouvray[40] deals, like other theoretical studies of the electronic structure of clusters, with a qualitative diagram of the Hückel MO of a polyhedral molecule. The novelty of this study consists in the analysis of the energies of the MO in a polyhedron of arbitrary type of symmetry solely on the basis of a scheme for the chemical bonds present in the molecule (i.e. the molecular graph). This approach is possible because the energies of the levels (i.e. the eigenvalues of the matrix of the model Hamiltonian H) in the Hückel model can be expressed in terms of the eigenvalues of another very simple matrix—the adjoint matrix A of the molecular graph whose elements are 1 for the pair of vertices

joined by a chemical bond and 0 for any other pair of vertices. The set of eigen-values of the adjoint matrix of a cyclic molecular graph C_n defines, for example, the MO diagram for aromatic π-systems, which constitutes the basis of the Hückel rule. The molecular orbital diagrams whereby it is possible to justify the $2n + 2$ rule can be derived analogously from the molecular graphs reflecting the bonding in the skeletal electron system of the cluster.

Starting with Wade's hypothesis of the involvement of three orbitals of the mononuclear fragment of a *closo*-polyhedron in the skeletal bonding system, it has been suggested[40] that two tangential orbitals (of the τ type), located along the tangent to the surface of the polyhedron, and one internal orbital (of the *i* type), directed to the centre of the cluster, be constructed from them. In an *n*-vertex cluster *n* bonding and *n* antibonding τ MO are formed from $2n$ τ AO, while a single bonding and $n - 1$ antibonding MO are formed from *n i* AO (the region of the mutual overlap of which is in the central part of the polyhedron) in conformity with the eigenvalues of the adjoint matrix of the graph of the *i* AO system, which represents the complete graph K_n (each vertex is connected to all the others). The bonding MO, the total number of which is thus $n + 1$, can accommodate $2n + 2$ skeletal electrons, which is consistent with Wade's rule. The cluster with triangular faces, which obeys the $2n + 2$ rule, is regarded as a three-dimensional superaromatic system with electron delocalisation, which represents a generalisation of the π-systems of planar aromatic molecules.

Thus, in addition to Wade's hypothesis of the separation of the exo- and endopolyhedral electron systems, the King and Rouvray scheme considers the τ and *i* MO also as independent of one another. These postulates appear to be fairly natural but cannot be rigorously derived from the symmetry properties of the cluster, which are altogether disregarded in this approach. The appearance of an additional pair of skeletal electrons in clusters with an open face has been justified[40] by introducing yet another hypothesis, this time the hypothesis of the separation of the system of *n i* AO of a *nido*-*n*-gon into the ν orbitals of the atoms surrounding the open face and the $n - \nu$ orbitals of the remaining atoms of the polyhedron. Each of these subsystems is assumed to be represented by its complete graph (K_ν and $K_{n-\nu}$ respectively), as a consequence of which two bonding orbitals of the *i* type arise in the system of skeletal MO instead of one such orbital. The increase of the number of open faces ("breaks") (on a *closo*-surface) as well as the introduction of "caps" in super-electron-deficient clusters lead, according to the authors,[40] to an increase of the degree of localisation of the bonds in the polyhedron.¶

Despite the importance of the results obtained, King and Rouvray's study[40] does not nevertheless provide an exhaustive description of three-dimensional superaromatic systems and does not contain a justification of the extremely significant initial postulates. The authors relate the degree of delocalisation of electrons in the cluster to the fraction of triangular faces on the total surface of the polyhedron, but the physical causes of this relation are not discussed. Finally, the results of graph theory have been applied in this instance only in terms of the simplest quantum-chemical Hückel method.

The strong aspects of the EHM are then clearly revealed: for example, it becomes understandable why calculations of this type have yielded such satisfactory results in the study of the polyhedral $B_nH_n^{2-}$ ions[27] but it has not been ultimately elucidated to what extent the relations obtained depend on the specific method of calculation employed.

Some of the questions enumerated above have been eliminated by Stone,[41] who developed a different much more general and physically well-founded model of the bonding interaction in the cluster. Having refrained from *a priori* assumptions about the number and form of the AO occupied in the exopolyhedral electron system, Stone employed in his study a single postulate, according to which the atoms making up the cluster polyhedron are approximately at equal distances from its centre. On this basis, he constructed a simple model of the polyhedral molecule whose atoms are uniformly distributed on the surface of a sphere. Thus, whereas the molecular symmetry is not considered at all in King and Rouvray's book, Stone's model has a spherical symmetry, which is the highest possible in a three-dimensional space. Nevertheless, with the aid of this model, it is possible to derive relations suitable for any clusters however low their symmetry.

In his study[41] Stone employed the wave function of a spherically symmetrical shell, which can be transformed into $R(r)Y_{lm}(\theta,\phi)$ in terms of polar coordinates, where the angular component Y_{lm} represents spherical functions, well known in quantum mechanics, which are defined in terms of two quantum numbers (the orbital momentum *l* and the magnetic momentum *m*) and which are degenerate by a factor $2l + 1$, like the sublevels of an isolated atom (see, for example, Messia[42]). Stone constructed the wave function of the cluster in accordance with the LCAO MO scheme in the form of a sum of the basis AO of the constituent atoms $\psi = \Sigma c_i\chi_i$; he employed the spherical functions Y_{lm} as the coefficients of the c_i in the expansion of ψ in terms of the basis functions $\{\chi_i\}$. This makes it possible to classify the resulting MO cluster in terms of the quantum number *l*, as is done for an isolated atom, by introducing the one-cluster *S* MO ($l = 0$), the three cluster *P* MO ($l = 1$), the five-cluster *D* MO ($l = 2$), etc. However, not all these MO exist in a specific cluster, because the spherical functions Y_{lm}, which appear in the expansion of the wave functions ψ for certain values of *l*, can become zero at the vertices of the polyhedron.

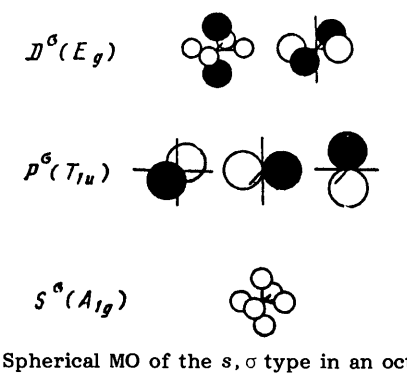


Figure 5. Spherical MO of the s,σ type in an octahedral cluster.[41]

In reality, only *n* linearly independent cluster MO can be made up of *n* basis functions χ_i. Thus it is possible to set up six independent MO of the σ type from six *s* AO of the metal atom (Fig.5): one fully symmetrical S^σ MO, three

¶The method developed by King and Rouvray[40] has been discussed in detail by Yanovskii (see this issue of the Journal). For our purposes, the use of postulates of a topological character in King and Rouvray's proof of the validity of the $2n + 2$ rule rather than the proof itself, is most significant.

degenerate P^{σ} MO antisymmetric with respect to inversion, and two of the five D^{σ} MO, since the other D^{σ} MO become zero (because the corresponding functions Y_{2m} at the vertices of the octahedron are zero).[41] The distribution of the cluster MO in terms of energy can be derived qualitatively from the number of nodal surfaces and is consistent with the usual pattern: the bonding A_{1g} MO, the non-bonding T_{1u} MO, and the antibonding E_g MO for an octahedral cluster (Fig. 4a).

The difference between the MO of a "spherical" cluster and the AO of an isolated atom consists in the fact that they have different forms depending not only on the quantum numbers l and m but also on the types of the basis functions (s, p, and d) and their overlap (σ, π, and δ). Accordingly, it is possible to isolate the following series of levels for a cluster made up to transition metal atoms: S_s^{σ}, P_s^{σ}, D_s^{σ}, ..., S_p^{σ}, P_p^{σ}, D_p^{σ}, ..., P_p^{π}, D_p^{π}, S_p^{π}, ..., P_d^{π}, D_d^{π}, F_d^{π}, ..., D_d^{δ}, δ_d, G_d^{δ}, ..., etc. The transition from cluster MO of the σ type to the MO of the π and δ types required also appropriate changes in the mathematical procedures, namely the introduction of the corresponding vector and tensor spherical functions instead of the corresponding scalar spherical functions Y_{lm}. The main consequence of such a change is the subdivision of $2n$ linearly independent π or δ MO into n low-energy even (i.e. symmetrical relative to the inversion operation) and n high-energy odd (antisymmetric in relation to inversion) orbitals. Thus pairs of MO made up of the even P_p^{π} and odd $\bar{P}_p^{\pi}$ orbitals, the even D_d^{δ} and odd $\bar{D}_d^{\delta}$ orbitals, etc., in which the first MO is in general bonding while the second is antibonding, appear.

Despite the large number of cluster MO of different types, their relative disposition as regards energy is extremely consistent. Thus, among all the MO of the σ type, only the S_s^{σ} orbital is bonding, while the others are antibonding. In the n-vertex cluster the P^{π} MO are divided into two groups: n even bonding P_p^{π} MO and n odd anti-bonding $\bar{P}_p^{\pi}$ MO, which is analogous to the formation of n molecular orbitals of the τ type and n orbitals of the τ^* type in the book of King and Rouvray. The cluster made up of n atoms of the elements in the Second Period thus contains $n + 1$ bonding MO. The splitting of the even and odd constituent π and δ MO, made up of d AO, is insignificant according to Stone's calculations[41] and all the MO of this type in the cluster are occupied by electrons (as shown above, the same result has been obtained in EHM calculations). Thus in this instance the $2n + 2$ rule has been justified (the presence of n bonding P_p^{π} MO and one bonding S_s^{σ} MO in the cluster). The expression for the bond energy in the cluster based on Stone's model contains a product of the type $Af(\omega)$, where $f(\omega)$ depends solely on the angular distance between neighbouring atoms on the surface of the sphere and the factor A is the ratio of the number of edges of the cluster to the number of its vertices and is a maximum for the *closo*-polyhedron with triangular faces. In this case the preference for cluster *closo*-structures is likewise well-founded.

At first sight Stone's scheme has no bearing on topology, because it uses the spherical shell model, which has been well developed in quantum mechanics. However, the very fact that the systematic treatment of the MO in accordance with the orbital quantum numbers l for an idealised spherical system is applicable to an arbitrary polyhedral molecule apparently demonstrates that the symmetry of the model is not itself of decisive importance in this instance and in a certain sense it merely complicates the description of the bonding, generating a large number of multiplets. Stone[41] emphasises the kinship between the spherical shell model and other simple models of systems with electron delocalisation—such as the linear potential box for conjugated polyenes and a closed conducting ring for cyclic π-systems. The latter model is purely topological: indeed Hückel's rule can be most simply derived for an ideal annular potential box with $D_{\infty h}$ symmetry (the lowest non-degenerate Σ_u level and an infinite sequence of doubly degenerate Π, Δ, etc. levels require the presence of $4n + 2$ π-electrons in a system with paired spins), but it is valid for all planar aromatic molecules however low their symmetry and is determined precisely by the fact that the π-electron system is closed. Analogously the adquacy of Stone's model in describing clusters is apparently determined by the same properties, namely the closed nature of the three-dimensional electron shell of the cluster, its homogeneous conductivity, and the presence of an inner cavity (we may note that the same properties of a superaromatic cluster with the additional hypothesis concerning the number of skeletal orbitals have been used in the studies by King and Rouvray).

In analysing cluster MO, Stone does not consider the consequences of the appearance of open faces in the polyhedron (i.e. the breakdown of the principle of the uniform distribution of atoms on the sphere underlying the model) and in essence proposes the same $2n + 2$ rule for every cluster, beginning with the diatomic molecule (as an example, he considered[41] the N_2 molecule). Despite the use of complex mathematical procedures, the scheme includes also significantly qualitative considerations, which are in many instances resorted to to account for the discrepancy between the predicted and true numbers of valence electrons in the molecule. The postulate of a weak interaction of the MO localised in various regions of the polyhedron (internal, surface, and exopolyhedral), which in fact corresponds to the postulate of the subdivision of the cluster MO into sybsystems (however, with a difference from the studies of Wade[2] and King and Rouvray[40] consisting in the fact that in Stone's work this postulate is a computational fact arising from the proposed model), is of special interest. The subdivision of the MO referring to topologically different regions of the cluster has been confirmed at the present time also experimentally;[9] however, quantum chemistry does not apparently as yet possess mathematical methods suitable for the analysis of this extremely interesting phenomenon.

Thus qualitative MO schemes make it possible not only to bring order into the experimental findings in the chemistry of clusters but also to achieve significant progress in the understanding of the causes of these findings. One may note further that principal advances in the theoretical description have been attained for clusters obeying the $2n + 2$ rule, which are nowadays regarded as three-dimensional superaromatic systems with a predominance of multicentre bonding. However, the electron count rules derived for such systems are applicable only to a limited range of skeletal compounds. In the next Section certain specific structures of metal clusters are considered in order to establish more definitely the limits of applicability of the qualitative theoretical structural schemes described above.

III. THE STRUCTURE OF TRANSITION METAL CLUSTERS

1. Trinuclear and Tetranuclear Clusters†

In these simplest polynuclear derivatives all the metal–metal bonds can be regarded as of the two-electron two-centre types; the magic numbers of the valence electrons of the

†The electronic structure of trinuclear metallocycles is examined in detail in S.P.Gubin's review (see this issue of the Journal).

cluster can therefore be determined in accordance with the EAN rule (Fig.1). The bonding and antibonding (in relation to the metal atoms) MO in these clusters are of course delocalised throughout the polyhedron, but they can be expressed mathematically by the combination of localised two-electron two-centre interactions. Many trinuclear and tetranuclear clusters of Group VI–VIII transition metals with carbanion π-olefin ligands obey the EAN rule (see, for example, Chini et al.[1] and Wade[2]).

However, in the present discussion we shall be interested in precisely those clusters which do not correspond to the commonest magic numbers and for this reason are more rarely dealt with in review communications. Certain representatives of the extremely numerous group of such compounds are compiled in Table 1, which also lists the principal characteristics of the cluster fragment in the molecule. Comparison of the M–M distances in the cluster and in the crystal lattice of the metal does not yield an unambiguous criterion for the existence (and even more so the multiplicity) of the metal–metal bond, although the sums of the Pauling metal atom radii are also listed in Table 1 to characterise the general trends in the variation of the interatomic distances.

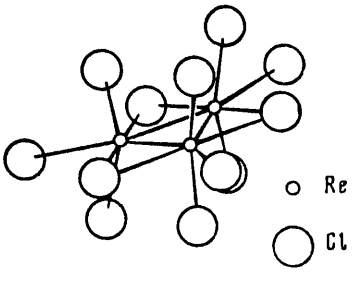


Figure 6. The structure of the $[Re_3(\mu_2\text{-}Cl)_3Cl_6]^{3-}$ cluster.[49]

Trinuclear and tetranuclear complexes of transition metals which do not obey the EAN rule can be arbitrarily divided into three non-equivalent groups. The first least numerous of these comprises clusters of the type $Os_3(CO)_{10}H_2$ in which the consequences of the deviation from the EAN rule can be readily interpreted within the framework of this same rule. Thus, the short Os–Os distance (2.680 Å) in $Os_3(CO)_{10}H_2$ can be attributed to a metal–metal double bond; multiplicities of 4/3 and 3/4 can be attributed to the Re–Re bonds (2.913 Å) in $Re_4(CO)_{12}H_4$ and the Ni–Ni bond (2.464 Å) in $Cp_4Ni_4H_3$ respectively; indeed, the average Re–Re distance (3.111 Å) in the 60-electron dianion $[Re_4(CO)_{12}H_6]^{2-}$ is greater by 0.20 Å than that observed in $Re_4(CO)_{12}H_4$.[47] The situation in the nickel derivative is somewhat more complex because the average Co–Co bond length in the 60-electron $Cp_4Co_4H_4$ cluster is 2.467 Å,[47] while the covalent radii of the cobalt and nickel atoms are similar; there exist also other nickel derivatives with an electron excess, for example, nickelocene, in which the presence of "superfluous" electrons does not lead to a structurally significant loosening of the bonds. The $Os_3(CO)_{10}H_2$ and $Re_4(CO)_{12}H_4$ clusters, which constitute an infrequent instance of the exception proving the rule, are regularly mentioned in theoretical studies.[2,23,25]

The trinuclear (Fig.6) complexes of Group II elements with halide and chalcogenide ligands of the type of $[Re_3Cl_{12}]^{3-}$ [49] or $[W_3O(OAc)_6(OH_2)_3]^{4+}$ [50] are discussed much more rarely in the literature devoted to the electronic structure of clusters. The number of valence electrons in these clusters (42ē) formally agrees with the existence of M=M double bonds, but such bonds in $[Re_3(\mu_2\text{-}Cl)_3Cl_9]^{3-}$ are shorter by 0.4 Å than the Re–Re bond in the dinuclear $H_2Re_2(CO)_8$ cluster (2.896 Å),[52] which can also be regarded as the double bond judging from the total number of electrons in the molecule. In terms of the "inorganic" (see above) electron counting scheme, the presence of double bonds has also been postulated in the trinuclear complexes considered.[49] Even more electron deficient clusters, for example $Re_3Cl_3(CH_2SiMe_3)_6$, in which the triangular $Re_3(\mu_2\text{-}Cl)_3$ fragment contains Re=Re double bonds 2.384–2.389 Å long according to the calculation based on the "inorganic" scheme, have been synthesised. However, according to the "organometallic" counting scheme, on the basis of the total number of valence electrons a multiplicity of 3 should be attributed to the same bonds. While it has certain advantages in the consideration of electronic structure, the existence of two electron counting schemes yielding inconsistent results nevertheless demonstrates that the description of the chemical bonds in clusters with halide and chalcogenide ligands has not been fully elaborated at the present time.

Table 1. Certain trinuclear and tetranuclear clusters not obeying the EAN rule.*

Formula	N_{val}	k_{M-M}	R (M–M), Å	R^M, Å	Refs.
$Os_3(CO)_{10}H_2$	46	3	2.81; 2.68	2.67	[44]
$Re_4(CO)_{12}H_4$	56	6	2.91	2.74	[45]
$Cp_4Ni_4H_3$	63	6	2.46	2.49	[46]
$[Re_3(\mu_2\text{-}Cl)_3Cl_9]^{3-}$	42	3	2.48	2.74	[49]
$[W_3(\mu_3\text{-}O)(\mu_2\text{-}OAc)_6(H_2O)_3]^{4+}$	42	3	2.75	2.74	[50]
$[Re_3Cl_3(CH_2SiMe_3)_6]$	36	3	2.39	2.74	[51]
$Pd_3(SO_2)_2[CN(t\text{-}Bu)]_5$	42	3	2.74	2.75	[53]
$Pt_3H_6[P(t\text{-}Bu)_3]_3$	42	3	2.82	2.77	[54]
$Pt_3[CN(t\text{-}Bu)]_6$	42	3	2.63	2.77	[55]
$Pt_3(CO)_3[P(C_6H_{11})_3]_4$	44	3	2.71	2.77	[56]
$Pd_3(CO)_3(PPh_3)_4$	44	3	2.72	2.75	[57]
$Pt_4H_2[P(t\text{-}Bu)_3]_4$	50	6	2.67; 2.80	2.77	[54]
$Pt_4H_8[P(iso\text{-}Pr)_2Ph]_4$	56	6	2.87; 3.08	2.77	[54]
$[Pd_4(phen)_4(CO)]_2^{4+}$	56	6	2.72; 2.89	2.75	[58]
$Pd_4(CO)_5(PPh_3)_4$	58	5	2.76	2.75	[57]
$Pt_4(CO)_5(PMe_2Ph)_4$	58	5	2.76	2.77	[59]
$Pd_4(CO)_6(PBu_3)_4$	60	6	2.78	2.75	[60]
$Cu_4(CH_2SiMe_3)_4$	48	4	2.42	2.55	[65]
$Cu_4(C_5H_4FeC_5H_5)_4$	48	4	2.44	2.55	[66]
$Ag_4(C_5H_4FeC_5H_5)_4$	48	4	2.74	2.88	[67]
$Cu_4[O(t\text{-}Bu)]_4$	56	0	2.71	2.55	[68]
$[Cu_4(SPh)_6]^{2-}$	64	0	2.76	2.55	[69]
$Cu_4(\mu_3\text{-}I)_4Py_4$	72	0	2.69	2.55	[70]
$[(C_5H_{11}N)AuCl]_4$	56	4	3.30	2.88	[71]
$Au_4(\mu_2\text{-}I)_2(PPh_3)_4$	58	6	2.74	2.88	[72]

*Notation: k_{M-M} is the number of metal–metal bonds in the cluster, R(M–M) the average metal–metal distance, and R^M the sum of the Pauling metal atom radii.[43]

The third and most varied group of "irregular" trinuclear and tetranuclear clusters consists of derivatives of pallidium, platinum, and copper subgroup metals. In contrast to the halide complexes, these clusters have recently attracted the attention of theoreticians,[23,33,35] but it would be premature at present to speak of the development of an electron counting scheme for such clusters. Certain analogues of magic numbers can be established empirically in palladium and platinum derivatives—they are usually smaller than in the corresponding complexes of the metals in the middle of the transition series, just as in the mononuclear derivatives of these elements the 16-electron shell is more stable than the 18-electron shell. Trinuclear 42- and 44-electron platinum and

palladium complexes, 56-electron tetrahedral clusters, and 58-electron clusters with the "butterfly" configuration are known (Table 1). The situation is complicated by the frequent deviations from these empirical magic numbers as well. Thus there exist the 50-electron tetrahedral $Pt_4.H_2[P(t\text{-}Bu)_3]_4$ and the 60-electron tetrahedral $Pd_4(CO)_6.[P(n\text{-}Bu)_3]_4$ clusters (the latter, included in Table 1, obeys the EAN rule in contradiction of the Table heading, which is more in the nature of an exception in the class of palladium and platinum derivatives). Assuming that the exopolyhedral Pt–Pt bonds in the pentanuclear $Pt_5(CO)_6(PPh_3)_4$ cluster (Fig.7) are two-electron two-centre bonds, we obtain yet another magic number—58ē for the Pt_4 tetrahedron.[61]

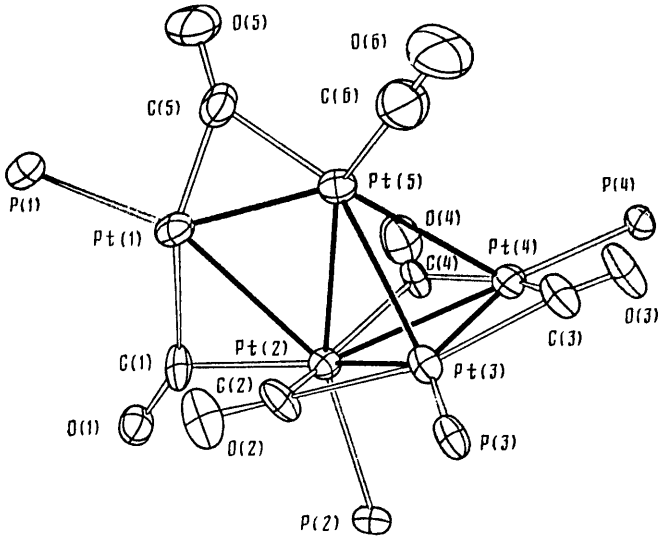


Figure 7. The $Pt_5(CO)_6(PPh_3)_4$ molecule (the phenyl substituents are not shown).[61]

The thermodynamically stable palladium and platinum clusters are able, in addition, to expand the coordination sphere of the metal atom, reacting under mild conditions with metallic mercury or its derivatives. Thus the bitetrahedral $\{[Ph(iso\text{-}Pr)_2P]_3Pt_3(CO)_3Hg\}_2$ cluster (Fig.8), which contains 54 or 53 electrons depending on whether the Hg...Hg contact 3.225 Å long is or is not regarded as a chemical bond,[62] the $[L_3Pt_3.(\mu_2\text{-}L)_3]_2Hg$ (where $L = Me_2C_6H_3NC$) *commo*-cluster of the sandwich type,[63] and the edge-condensed $Pd_4Hg_2Br_2(\mu_2\text{-}CO)_4.(PEt_3)_4$ cluster[64] have been obtained. Their electronic structure is difficult to interpret at the existing level of theoretical ideas.

The structures of the tetranuclear copper, silver, and gold complexes are even less susceptible to classification. The existence of the planar M_4 tetragon, which exhibits a tendency towards the formation of four additional M...Fe bonds in the ferrocenyl derivative $Cu_4(C_5H_4FeC_5H_4R)_4$ ($R = CH_2.NMe_2$) [66] (and in its silver analogue[67]), is characteristic of copper derivatives. The Cu–Cu distance in the 56-electron $Cu_4[O(t\text{-}Bu)]_4$ cluster (parallelogram) and in the 64-electron $[Cu_4(SPh)_6]^{2-}$ cluster (tetrahedron) is greater than in the formally 72-electron $Cu_4(\mu_3\text{-}I_4)Py_4$ complex, where metal–metal bonds should be absent according to the EAN rule. The Cu–Cu distances in the isoelectronic cubane-like clusters of the latter type vary in the range 2.65–3.21 Å.[70] The Cu–Cu contacts 2.6–2.8 Å long are not usually assumed to correspond to a direct metal–metal interaction.[68–70]

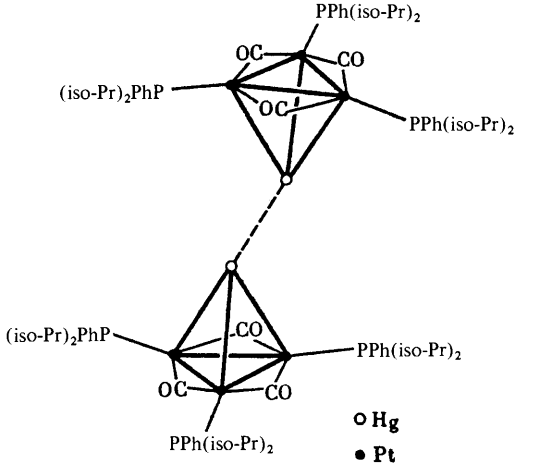


Figure 8. The $\{[Ph(iso\text{-}Pr)_2P]_3Pt_3(CO)_3Hg\}_2$ cluster (the hydrocarbon fragments are not shown).[62]

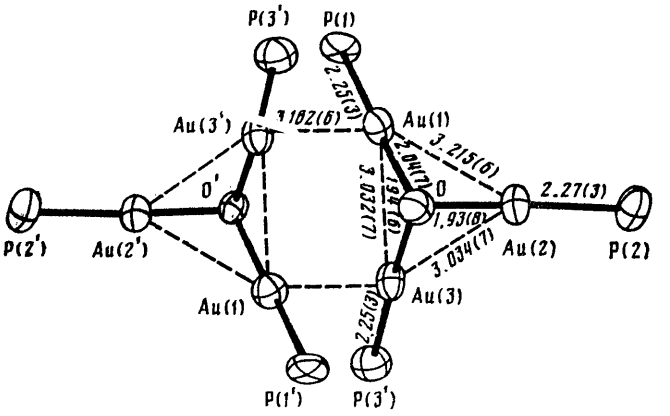


Figure 9. The structure of the $[(Ph_3PAu)_3O]_2^{2+}$ cation[74] (the phenyl substituents are not shown).

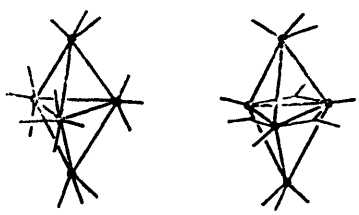
Somewhat in contrast to this, the gold derivatives definitely manifest a tendency towards a weak "secondary" Au...Au interaction at distances of 3.0–3.5 Å, which is observed, for example, in $C_5H_{10}NAuCl_4$.[71] The $Au_4(\mu_2\text{-}I)_2(PPh_3)_4$ structure contains the 58-electron Au_4 tetrahedron, while the formally 56-electron Au_4 tetrahedron in the pentanuclear $[Au_5(PPh_2.CH_2PPh_2)_3CH(PPh_2)_2]^{2+}$ dication is linked via one of its vertices to the 14-electron linearly coordinated Au atom.[73] Finally, two 42-electron $(LAu)_3E^+$ cations in the series of $[(LAu)_3E]_2^{2+}$ dimers (where $L = PPh_3$ and E = chalcogen atom[74,75]) are linked in pairs by secondary Au...Au interactions over distances of 3.15–3.40 Å (Fig.9).

We believe that the data examined suggest that the trinuclear and tetranuclear clusters of post-transition metals, palladium, and platinum do not on the whole exhibit an

unambiguous relation between the geometrical characteristics of the polyhedra present in their molecules and the numbers of valence electrons.

2. Trigonal-Bipyramidal Clusters

The trigonal-bipyramidal fragment is believed to be the first "Wade" *closo*-polyhedron and exists as such in the structures of a series of clusters satisfying the $2n + 2$ rule (Table 2, left half). According to this rule, clusters with 12 skeletal electrons, made up of the atoms of transition or non-transition elements are analogues of the *closo*-carbaborane $C_2B_3H_5$ (Fig.10). A characteristic feature of structures of the trigonal-bipyramidal type is, however, their intermediate position between polyhedra with localised and many-centre bonds, because the trigonal bipyramid can be equally well regarded as a one-cap tetrahedron, the localised bonding in which also requires twelve electrons. As a consequence of this, derivatives of the type $Os_4(CO)_{12}NMe$, for example, where the M_4 is a tetrahedron coordinated via a triangular face to the μ_3-NMe ligand, the M_4C or M_4N "butterfly" in which a non-metal atom is incorporated, or the M_3 triangle and two μ_3-X ligands, are sometimes classified as mixed trigonal-bipyramidal clusters.



a *b*

Figure 10. Examples of the "Wade" (*a*) and "non-Wade" (*b*) trigonal-bipyramidal clusters and the numbers of skeletal electrons in the latter: *a*) $Os_5(CO)_{16}$, $12\bar{e}$; *b*) $[Ni_5(CO)_{12}]^{2-}$, $16\bar{e}$.

This kind of borderline position of trigonal-bipyramidal structures is also expressed by the existence among them of a large number of exceptions to the $2n + 2$ rule (Table 2, right half) and these exceptions cannot at present be confidently ascribed to the presence in the polyhedron of the atoms of a post-transition element. The $[PtRh_4(CO)_{12}]^2$ ($12\bar{e}$) and $[PtRh_4(CO)_{14}]^{2-}$ ($16\bar{e}$) mixed clusters exhibit, for example, an isomeric behaviour of the cluster nucleus which depends on whether the Pt atom occupies the apical or equatorial position.

The characteristic features of the trigonal-bipyramidal complexes made it necessary to postulate the existence in them of two magic numbers (12 and 16) of skeletal electrons or (for clusters made up of transition metal atoms) of 72 and 76 valence electrons.[22,88] The experimentally observed increase in the length of the equatorial-apical metal–metal bonds compared with the equatorial-equatorial bonds in the 76-electron derivatives has been explained with the aid of EHM calculations.[22] However, Table 2 shows that there exist also clusters with ten and fourteen skeletal electrons. Among the polynuclear complexes of metals of the iron and cobalt subgroup trigonal bipyramidal derivatives are encountered much more rarely than the octahedral complexes.

3. Derivatives of Octahedral Clusters

The $2n + 2$ rule holds most rigorously for the octahedral clusters of transition metals of the iron and cobalt subgroups with carbonyl ligands, some of which can be substituted by other "soft" ligands (η^n-olefin, phosphine, and nitrosyl ligands). The examples in Table 3 show that the polyhedron in these clusters can consist of atoms of different elements [the heteronuclear $Ru_4C_2Me_2(CO)_{12}$ complex (Fig.11), in which the $Ru_4(CO)_{12}$ "butterfly" has been built onto the octahedron via the acetylene ligand of the complex bridging functional group is especially interesting[92]] or can incorporate a C or H atom within the cavity of the polyhedron. It is noteworthy that even the $Cp_6Ti_6O_8$ titanium cluster with μ_3-oxo-bridges and the heteronuclear carbide cluster $(Et_3PAu)_2.Fe_4C(CO)_{12}$ each have 14 skeletal electrons, differing in this respect from the majority of the polynuclear compounds at the beginning and end of the transition series which have been investigated. Pentanuclear *nido*- and *arachno*-derivatives which can be synthesised from octahedral clusters, are also known. Thus a 14-electron tetragonal pyramid can be obtained by removing one vertex of the octahedron (this leads to a general method of synthesis of heteronuclear clusters, as a result of the successive introduction of atoms of other transition elements in place of the missing vertex[94]), while a 16-electron *arachno*-cluster can be obtained by adding two-electron donors to the corresponding *nido*-derivatives (Fig.12).

Table 2. Examples of trigonal-bipyramidal clusters.†

Formula	N_{sk}	Refs.	Formula	N_{sk}	Refs.
$C_2B_2H_5$	12	[76]	$Ph_3PAuRu_3Co(CO)_{11}$	10	[83]
Sn_5^{2-}	12	[77]	$Cp_2Cr_2Co(\mu_3\text{-}S)_2[\mu_2\text{-}$	10	[84]
$Os_5(CO)_{16}$	12	[78]	$\text{-}S(t\text{-}Bu)](CO)_2$		
$[PtRh_4(CO)_{12}]^{2-}$	12	[79]	$Cp_5V_5O_6$	14	[85]
$Os_4(CO)_{12}(\mu_3\text{-}NMe)$	12	[80]	$Cp_3Co_3(\mu_3\text{-}S)_2$	14	[86]
$HRu_4N(CO)_{11}P(OMe)_3$	12	[81]	$[RuIr_4(CO)_{15}]^{2-}$	16	[79]
$[Ni_3S_2(PEt_3)_6]^{2+}$	12	[82]	$[Ni_5(CO)_{12}]^{2-}$	16	[87]
			$[PtRh_4(CO)_{14}]^{2-}$	16	[79]
			$Cp_3Ni_3(\mu_3\text{-}S)_2$	17	[88]

†N_{sk} is the number of skeletal electrons in the cluster.

Table 3. The "Wade" octahedral clusters of Group IV–VIII transition metals and their derivatives.

Formula	N_{val}	N_{sk}	R (M–M), Å	R^M, Å	Refs.
$Rh_6(CO)_{16}$	86	14	2.78	2.68	[13]
$[Co_6H(CO)_{15}]^-$	86	14	2.58	2.48	[89]
$Ru_6C(CO)_{14}(C_6H_3Me_3)$	86	14	2.88	2.65	[90]
$Cp_6Ti_6O_8$	86	14	2.89	2.98	[91]
$Ru_4C_2Me_2(CO)_{12}$	66	14	2.75	2.65	[92]
$(Et_3P)_2Au_2Fe_4C(CO)_{12}$	86	14	2.92 (Fe—Au) 2.65 (Fe—Fe) 3.02 (Au—Au)	2.88 (Au) 2.49 (Fe)	[93]
$HFe_5N(CO)_{14}$	74	14	2.58	2.49	[95]
$Ru_5C(CO)_{15}NCMe$	76	16	2.85	2.65	[96]
Cp_6Ni_6	90	18	2.42	2.49	[97]
$[Fe_6S_8(PEt_3)_6]^{2+}$	90	18	2.62	2.49	[98]

The cyclopentadienylnickel cluster Cp_6Ni_6 (its monocation is also known[97]) and the iron cluster[98] $Fe_6S_8(PEt_3)_6$ with phosphine and μ_3-sulphide ligands, in which there is a significant loosening of the metal–metal bonds, are exceptions to Wade's

rule. It is of interest to note that, in contrast to its analogues in the Periodic System, clusters with an electron excess are fairly characteristic of nickel, namely $Cp_4Ni_4H_3$,[46] $[Ni_5.(CO)_{12}]^{2-}$,[87] and Cp_6Ni_6.[97]

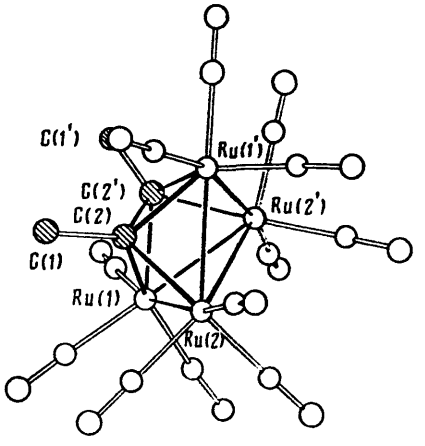


Figure 11. The structure of $Ru_4C_2Me_2(CO)_{12}$.[92]

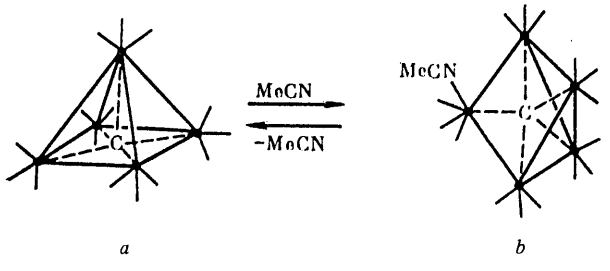


Figure 12. The interconversions of the *nido*- and *arachno*-clusters of ruthenium: *a*) $Ru_5C(CO)_{15}$, 14ē; *b*) $Ru_5C(CO)_{15}.(MeCN)$, 16ē.

Among octahedral clusters, there exist also numerous "non-Wade" derivatives, including, in particular, the halide complexes of Group III-VI transition metals (Table 4). The $M_6(\mu_2\text{-}X)_{12}$ and $M_6(\mu_3\text{-}X)_8$ motifs, where the halogen atoms form bridges along all the edges or along all the faces of the octahedron with additional apical coordination of the ligands to its vertices, occur widely in these clusters, which are distinguished by a fixed configuration of the ligand environment relative to the metallopolyhedron. The chemical bonds in the cluster nuclei of such compounds are usually described qualitatively in terms of the "inorganic" electron counting scheme which is not identical to the "organometallic" scheme adopted in this review.

Wade attempted to combine the two approaches[2] by postulating the involvement of four AO from each metal atom in skeletal bonding in "non-Wade" clusters. The bonds in the $[Nb_6(\mu_2\text{-}Cl)_{12}]^{2+}$ and $[Mo_6(\mu_3\text{-}Cl)_8]^{4+}$ model clusters are then assumed to be respectively two-electron three-centre bonds (eight bonds, 16ē) or two-electron two-centre bonds (twelve bonds, 24ē). Apart from the reduction of the predictive power of such a model as a consequence of the introduction of bonds with different degrees of localisation into isotypical compounds, one should note that the formal charge separation in the molecule by no means allows the isolation of the cluster fragments of the above types in all the existing octahedral metal complexes with halide ligands.

Table 4. Cluster transition metal halides.

Formula*	N_{val}	R (M—M), Å	R^M, Å	Refs.
$Zr_6(\mu_2\text{-}I)_{12}$	72	3.20	3.13	[99]
$[Nb_6(\mu_2\text{-}Cl)_{12}Cl_6]^{2-}$	74	3.02	2.85	[100]
$Nb_6(\mu_2\text{-}Cl)_{12}(Cl_{4/2})$	75	2.92	2.85	[101]
$[Ta_6(\mu_2\text{-}Cl)_{12}(CN)_6]^{4-}$	76	2.93	2.85	[102]
$W_6(\mu_2\text{-}Cl)_{12}Cl_6$	78	2.92	2.74	[103]
$[Nb_6(\mu_3\text{-}I)_8(I_{6/2})]^-$	80	2.83	2.85	[104]
$Mo_6(\mu_3\text{-}Cl)_8Br_6]^{2-}$	84	2.62	2.72	[105]

*The fractional subscripts correspond to compounds in the crystals of which the vertices of two neighbouring clusters are linked by bridging halide ligands.

The evaluation of the number of valence electrons in the metallopolyhedra of the compounds listed in Table 4 suggests that a characteristic feature of these polynuclear complexes is the absence of magic numbers as such rather than the existence of magic numbers (they could be found empirically from the available experimental data) other than in the carbonyl clusters. We believe that the reason for this may lie in the "super-electron deficiency" of the cluster derivatives of metals at the beginning of the transition series as a result of which the corresponding metallopolyhedron is coordination-saturated even before its ability to receive the electrons supplied by the ligand has been exhausted, i.e. before all its low-energy CVMO have been occupied. It is noteworthy that the $Cp_6Ti_6O_8$ cluster with many-electron ligands satisfies the $2n + 2$ rule.[91]

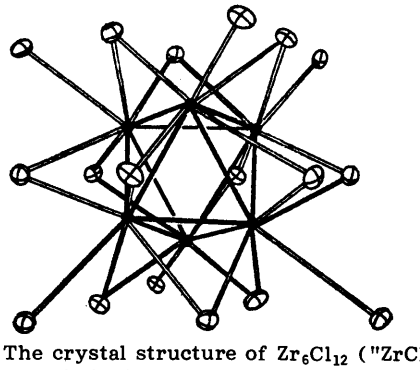


Figure 13. The crystal structure of Zr_6Cl_{12} ("$ZrCl_2$"). The metallopolyhedron is indicated; the Cl atoms in the equatorial belt are coordinated to the vertices of neighbouring octahedral clusters.

Yet another feature of the cluster transition metal halides is the breakdown of the principle of the uniform occupation of the coordination sphere of the metallopolyhedron by ligands,

which is valid for the corresponding carbonyl analogues.[6] Thus an arrangement of Cl ligands in layers is observed (Fig.13) in the Zr_6Cl_{12} structure, while the μ_2-Cl ligands in the equatorial component of the coordination shell are additionally coordinated along the vertices of neighbouring octahedra. The structural motifs examined are also common in organic clusters with chalcogenide ligands (Chevrel phases); metallo-octahedra with a mixed halide-chalcogenide environment are also known.

Derivatives of post-transition metals constitute yet another group of non-Wade octahedral clusters by analogy with the trinuclear and tetranuclear structures which do not obey the EAN rule. Few structural studies have so far been made on polynuclear compounds of this class, where (Table 5) the absence of magic numbers rather than an appreciable preference for particular electronic configurations is to be seen in the cluster halides of metals at the beginning of the transition series. The ammine, phosphine, and σ-aryl (more rarely σ-alkyl) groups are characteristic ligands for the elements of the copper subgroup.

Table 5. Hexanuclear clusters of post-transition elements.

Formula	N_{val}	N_{sk}	R (M–M), Å	r^M, Å	Refs.
$Ir_2Cu_4(\sigma,\eta\text{-}C{\equiv}CPh)_8(PPh_3)_2$	90	18	2.74 (Cu—Cu) 2.87 (Cu—Ir)	2.52 (Cu) 2.71 (Ir)	[106]
$H_6Cu_6(PPh_3)_6$	84	12	2.60	2.55	[107]
$Cu_6(o\text{-}Me_2NC_6H_4)_4(\mu_2\text{-}Br)_2$	84	12	2.61	2.55	[108]
$Cu_4(o\text{-}Me_2NC_6H_4)_4(\mu\text{-}C_2Ph)_2$	80	8	2.58	2.55	[109]
$[Ag_6[S_2C{=}C(CN)_2]_6]^{6-}$	96	24	3.04	2.88	[110]
$[Au_6(PTol_3)_6]^{2+}$	76	4	3.02	2.88	[30]
$Au_6(PPh_3)_4[Co(CO)_4]_2$*	76	4	2.75	2.88	[111]
$[(Ph_3P)_2Au_3(\mu_3\text{-}O)]_2^{2+}$	84	12	3.11	2.88	[74]

*The $Co(CO)_4$ fragments play the role of ligands, forming exopolyhedral Au–Co bonds.

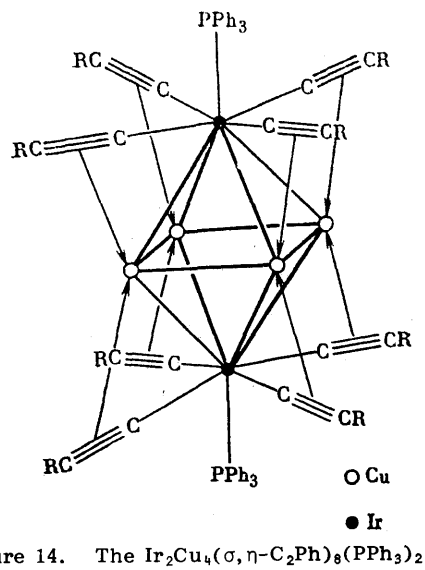


Figure 14. The $Ir_2Cu_4(\sigma,\eta\text{-}C_2Ph)_8(PPh_3)_2$ cluster.

Thus the $Ir_2Cu_4(C_2Ph)_8(PPh_3)_2$ cluster (Fig.14) contains 18 skeletal electrons, if each σ,π-acetylide is regarded as the donor of five electrons, or proves to be super-electron-deficient if it is assumed that these ligands each supply three electrons (this is more usual in the case of one-centre π-coordination of alkynes). The task of explaining the existence, inconsistent with calculated data, of the octahedral $[Au_6(PTol_3)_6]^{2+}$ (Tol = *p*-tolyl) cluster and the isoelectronic bitetrahedral $Au_6(PPh_3)_4[Co(CO)_4]_2$ cluster is made still more difficult by the presence of a bitetrahedral configuration, analogous to that in the latter cluster, in the 82-electron polyhedron (discussed above) in $Pd_2Hg_2Br_2(CO)_4(PEt_3)_4$. On the other hand, dications of the type $[(Ph_3PAu)_3E]_2^{2+}$ (E = S, Se, or Te—see Fig.9), which are isoelectronic with the octahedral copper clusters $H_6Cu_6(PPh_3)_6$ and $Cu_6(o\text{-}Me_2NC_6H_4)_4(\mu_2\text{-}Br)_2$, contain an open tricyclic Au_6 skeleton. Finally, distorted Ag_6 octahedra with Ag...Ag contacts 3.01 and 3.74 Å long, which are a general characteristic of polynuclear silver compounds normally containing complex polyatomic skeletons, are present in the $\{Ag_6[S_2C{=}C(CN)_2]_6\}^{6-}$ structure.[110]

Table 6. Clusters of medium size.

Formula	Reference polyhedron	No. of caps	N_{val}	N^{val}_{CVMO}	N_{sk}	$N^{sk}_{(2n+2)}$	Refs.
$[Rh_7(CO)_{16}]^{3-}$	Octahedron	1	98	98	14	14	[112]
$[Os_8(CO)_{22}]^{2-}$	"	2	110	110	14	14	[113]
$[Re_6C(CO)_{24}]^{2-}$	"	2	110	110	14	14	[114]
$[Os_{10}C(CO)_{24}]^{2-}$	"	4	134	140	14	14	[29]
$Pd_7(CO)_7(PMe_3)_7$	"	1	98	98	14	14	[116]
$Pd_{10}(CO)_{12}[P(n\text{-}Bu)_3]_6$	"	4	136	140	16	14	[60]
$Hg_6Rh_6(PMe_3)_6$	"	4	132	140	12	14	[117]
$[Pd_6Fe_6(CO)_{24}H]^{3-}$	"	6	160	166	16	14	[118]
$[Rh_9(CO)_{19}]^{3-}$	Two octahedra with common face	0	122	124	14	14	[121]
$[Ru_{10}(C)_2(CO)_{24}]^{2-}$	Two octahedra with common edge	0	138	130	18	18	[122]
$[Rh_{11}(CO)_{23}]^{3-}$	Three octahedra with common faces	0	148	—	16	14	[124]
$[Rh_9P(CO)_{21}]^{2-}$	Tetragonal antiprism	1	130	130	22	22	[125]
$[Rh_{10}S(CO)_{22}]^{2-}$	Ditto	2	142	142	22	22	[127]
$[Sn_9Tl]^{3-}$	"	2	42	—	22	22	[128]
$[Co_8(CO)_{18}C]^{2-}$	"	0	114	114	18	22	[129]
$[PtRh_{10}N(CO)_{22}]^{3-}$	Trigonal prism	5	150	146	18	20	[132]
$[Bi_9]^{5+}$	Ditto	3	40	—	22	20	[133]
$[Rh_{12}Sb(CO)_{27}]^{3-}$	Eicosahedron	0	170	170	26	26	[135]

Notation: N_{val} is the number of valence electrons in the cluster, N^{val}_{CVMO} the number of valence electrons calculated in accordance with Lauher's scheme, N_{sk} the number of skeletal electrons in the cluster, and $N^{sk}_{(2n+2)}$ the number of skeletal electrons predicted by Wade's rule.

Evaluation of the number of skeletal electrons in fairly representative groups of clusters with an octahedral structure based on different transition and post-transition elements thus demonstrates a consistent character of the electronic structure in derivatives of metals in the middle of transition series and the apparent absence of such regularities in clusters of the elements at the beginning and end of the transition series. The causes of the failure of the magic number (2*n* + 2) rule for elements to the left and right of Fe and Co as well as their analogues are evidently various, but we believe that the very fact of such behaviour of metal clusters reveals a close relation between the 2*n* + 2 and EAN rules, because the regions of their applicability in the series of transition elements are virtually identical.

4. Clusters Based on Polyhedra of Medium Dimensions

Metal clusters containing M_n polyhedra with a number of vertices n between 7 and 12 will be assigned to this group of polynuclear compounds. Most of such clusters consist of osmium and rhodium derivatives; cobalt, palladium, and gold compounds have also been investigated. Table 6 presents examples of such clusters; the numbers of their valence electrons are compared with the numbers found in accordance with the $2n + 2$ rule and calculated on the basis of the CVMO scheme.[22-24] Among the compounds considered, it is possible to differentiate several types of structures differing in the "reference" polyhedra which can have one or several caps. We shall consider subsequently the polyhedra of each type in order of increasing complexity of their reference polyhedron.

(a) Octahedra with centred faces. Clusters of this type have no analogies in the structures of boranes and carbaboranes. According to the $2n + 2$ scheme, the addition of a cap (i.e. a vertex over the centre of a triangular face) to an octahedral cluster does not increase the number of skeletal electrons of the octahedron. Accordingly, in the known clusters of metal-analogues, namely manganese, iron, and cobalt, having the structures of one-, two-, and four-cap octahedra, the magic number of skeletal electrons $N_{sk} = 14$ obtains. The electronic structure of the ten-vertex cluster $[Os_{10}C(CO)_{24}]^{2-}$,[29] which cannot be interpreted within the framework of the CVMO scheme on the basis of the results of EHM calculations, is in reality rigorously consistent with Wade's rule, which has been confirmed in a series of recent studies on derivatives of clusters of this type.[115]

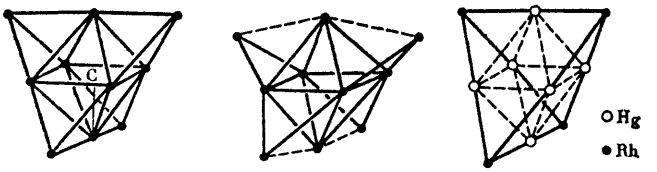


Figure 15. Decagonal clusters with a four-cap octahedron made up of metal atoms and the numbers of skeletal electrons in them: *a*) $[Os_{10}C(CO)_{24}]^{2-}$, 14$\bar{e}$;[29] *b*) $Pd_{10}(CO)_{12}(PBu_3)_6$, 16$\bar{e}$;[60] *c*) $Hg_6Rh_4(PMe_3)_{12}$, 12$\bar{e}$.[117]

Deviations from Wade's rule appear in the analogous palladium derivatives: the observed "opening of caps" requires the appearance of additional electrons relative to the closed electronic configuration, namely two in $Pd_7(CO)_7(PMe_3)_7$ and eight in $Pd_{10}(CO)_{12}[P(n\text{-}Bu)_3]_6$, which is inconsistent with the real numbers of valence electrons in these clusters. The number $N_{val} = 160$ in the dodecanuclear cluster $[Pd_6Fe_6.(CO)_{24}H]^{3-}$ [118] corresponds to $N_{sk} = 16$, which is inconsistent with the $2n + 2$ rule, but can be reproduced in terms of the CVMO scheme; at present it is not entirely clear whether the observed distortions of the trigonal-antiprismatic type in the internal Pd_6 octahedron are a result of the deviation from Wade's magic number $N_{sk} = 14$. For the $Hg_6Rh_4.(PMe_3)_{12}$ cluster, the establishment of a correlation between the number of electrons and the geometrical characteristics of the polyhedra constitutes a still more difficult task. Examples of decanuclear clusters (Fig.15) illustrate yet again the loss of predictive power by Wade's rule for clusters of metals at the end of the transition series.

(b) Polyoctahedral clusters. The $2n + 2$ rule can apparently be extended (provided that it is valid for the constituent polyhedra) to clusters consisting of two or several polyhedra having common vertices (*commo*-clusters, polyhedra with a common edge and a common face); by relating the number of skeletal electrons in such compounds to the number of non-common vertices, i.e. vertices which do not belong simultaneously to two or several polyhedra. Accordingly, the numbers of skeletal electrons in the recently synthesised $[Rh_9(CO)_{19}]^{3-}$ and $[Ru_{10}(C)_2(CO)_{24}]^{2-}$ clusters and also in the mixed cluster $Os_6C(CO)_{16}(C_2Me_2)$[121] are analogous to those required for the corresponding *closo*-hexagon, *closo*-octagon, and *arachno*-hexagon (Fig.16).

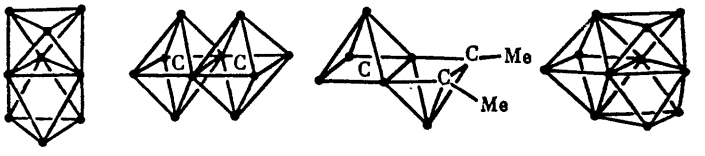


Figure 16. Polyoctahedral clusters and the numbers of skeletal electrons observed in them: *a*) $[Rh_9(CO)_{15}]^{3-}$, 14$\bar{e}$;[121] *b*) $[Ru_{10}(C)_2(CO)_{24}]^{2-}$, 18e;[122] *c*) $Os_6C(CO)_{16}C_2Me_2$, 18$\bar{e}$;[123] *d*) $[Rh_{11}(CO)_{23}]^{3-}$, 16$\bar{e}$.[124]

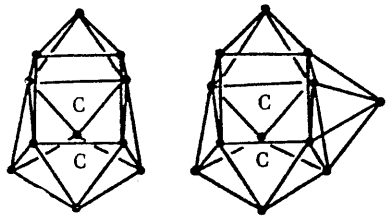
A more general rule for the calculation of the magic numbers of valence electrons for any multipolyhedral clusters has now been proposed by Mingos;[120] the total magic number of valence electrons of the cluster is equal to the sum of the magic numbers of its constituent polyhedra minus the sum of the magic numbers of the boundary fragments (18$\bar{e}$ for a single atom in *commo*-clusters, 34$\bar{e}$ for two atoms located on a common edge of the cluster, and 48$\bar{e}$ for three atoms on a common triangular face or 50$\bar{e}$ for a common face in polyhedra with electron delocalisation). Mingos's rule makes it possible, for example, to obtain the magic number of valence electrons in a trigonal bipyramid regarded as two tetrahedra with a common fact ($60 + 60 - 48 = 72\bar{e}$) and is valid for a large number of clusters of a wide variety of types.# We may recall that the numbers of valence and skeletal electrons in the cluster differ by $12n$, where n is the number of atoms in the cluster.

It is noteworthy that Wade's magic numbers characterise a trend rather than a rigorous rule in the geometrical structures of clusters in the case of compound polyhedra: thus the distances between the apical atoms of the two octahedra in $Ru_{10}(C)_2(CO)_{24}]^{2-}$ not linked by valence forces (Ru...Ru contacts 3.112 and 3.138 Å long) exceed only slightly the

#Analogous rules have been proposed in a recent study by Mingos and Evans[148] for platinum clusters. In this case the magic numbers of boundary fragments are 16$\bar{e}$ for a common vertex, 30$\bar{e}$ for a common edge, and 44$\bar{e}$ for a common triangular face. For the pentanuclear cluster $Pt_5(CO)_6(PPh_3)_4$, the scheme predicts the number 70$\bar{e}$, which agrees with the true number (see, however, Section III, 2 of the present review).

lengths of certain edges (2.803–3.098 Å). However, the CVMO scheme yields for these clusters numbers of valence electrons which are inconsistent with the observed numbers.[24] The trisoctahedral cluster having the composition $[Rh_{11}(CO)_{23}]^{3-}$ indicated in Table 6 deviates from the 2*n* + 2 rule; calculations of its electronic structure on the basis of the CVMO scheme have not been carried out. The presence of five long edges (2.96–3.06 Å) in the Rh_{11} polyhedron has been rationally explained [124] by the deformation of its constituent condensed octahedra, because in this case octahedra do not fill the three-dimensional space.

(c) Clusters based on a tetragonal (Archimedes) antiprism. The recently synthesised derivatives of this type with one (*nido*-M_9) or two (*closo*-M_{10}) caps over the "open" tetragonal faces of the reference polyhedron contain 22 skeletal electrons in conformity with the 2*n* + 2 rule. The inner cavity of the rhodium clusters contains P, S, or As atoms. It is of interest that the specific metal–metal distances in this group of clusters can vary within fairly wide limits (particularly in the polyhedral anions Sn_8Tl^{3-} and Sn_9Tl^{3-}).[128] In essence, on the basis of the 2*n* + 2 rule, it is possible to predict in compounds of the given type only an idealised configuration of the polyhedron, which in the real structure may undergo considerable distortions. It is noteworthy that in the carbaborane derivatives of analogous structure the 2*n* + 2 rule holds extremely rigorously.[2]



a *b*

Figure 17. *a*) $[Co_{11}C_2(CO_{22})]^{3-}$; *b*) $Rh_{12}C_2(CO)_{25}$.

(d) Polyhedra with an irregular structure. We understand this term to mean metal clusters of complex form in the structures of which it is possible to isolate the reference polyhedron only tentatively. Such compounds are usually characterised by fairly significant deviations from the 2*n* + 2 rule. The $[Co_8C(CO)_{18}]^{2-}$ cluster occupies an intermediate position between those examined in the present and previous Sections: it has a tetragonal antiprismatic type of structure, but, as a consequence of distortion, it is also close to a two-cap trigonal prism (one of the open faces of the antiprism is "pierced" by the Co...Co contact 3.225 Å long); the number of skeletal electrons in this cluster does not agree with Wade's rule (but is correctly reproduced in terms of the CVMO scheme[22]). The distortions of the polyhedron considered have been explained[1] as a result of the discrepancy between the covalent radius of the carbon atom (0.77 Å) and the somewhat larger internal cavity in clusters of the tetragonal-antiprismatic type (capable of incorporating the atoms of non-metals in the Third and Fourth Period, as can be seen from the previous Section).

The undecanuclear $[Co_{11}C_2(CO)_{22}]^{3-}$ cluster[130] and the dodecanuclear $Rh_{12}C_2(CO)_{25}$ cluster[131] (Fig.17), containing in the inner cavities the diatomic C_2 group with C–C distances of 1.62 and 1.48 Å respectively, are even less susceptible to an "idealised" description. In the complex polyhedra of these clusters, each of which has two open tetragonal faces, there are 22 skeletal electrons in each case, i.e. the number N_{sk} characteristic of a *closo*-decagon holds. The presence of open faces thus ceases to affect the total number of skeletal electrons, which also remain unchanged following the appearance of a cap over each face.

The heteronuclear nitride cluster $[PtRh_{10}N(CO)_{21}]^{3-}$ can be represented by a three-cap trigonal prism with two additional caps, each of which constitutes simultaneously the centre of two rectangular faces; however, the lateral edges of such a prism are lengthened up to "non-bonding" Rh...Rh distances and amount to ~3.50 Å (Fig.18). The super-electron-deficient metalloborane and metallocarbaborane clusters have an analogous structure (see Yanovskii's review in this Journal).

Distortions of the type indicated are a general characteristic of trigonal-prismatic clusters with caps, which can be illustrated by the structure of Bi_9^{5+}.[133] In this polynuclear cation the lateral edges of the reference prism have been lengthened to 3.704–3.979 Å, while the other Bi–Bi distances in the polyhedron are in the range 3.078–3.286 Å. The number of electrons in Bi_9^{5+} is greater than the Wade number by 2, which is consistent with the predictions of the CVMO scheme for rhodium clusters.[22]

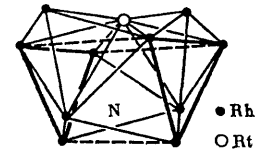


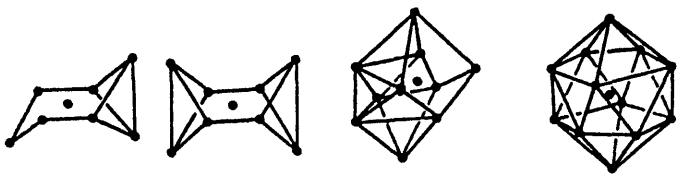
Figure 18. The $[PtRh_{10}N(CO)_{21}]^{3-}$ cluster[132] (the reference polyhedron is indicated).

(e) Clusters based on a centred eicosahedron. Among carbaboranes and metallo-carbaboranes, eicosahedral derivatives constitute the largest class which is most consistent with the 2*n* + 2 rule.[134] On the other hand, with increase of the size of the polyhedron in metal clusters a tendency arises towards the breakdown of this rule. In the single structurally investigated distorted eicosahedral rhodium cluster $[Rh_{12}Sb(CO)_{27}]^{3-}$ the inner cavity is occupied by an Sb atom (the Sb–Rh distances are 2.712 and 2.922 Å) and, for the average Rh–Rh bonding distance in the polyhedron of 2.912 Å, three edges of the cluster are extended to 3.334 Å.[135] Despite the existence of "semiopen" faces, the cluster contains 26 skeletal electrons, which is typical for a *closo*-eicosahedron. The closeness of the covalent radii of the Sb (1.36 Å) and Rh (1.32 Å) atoms[43] is responsible for the possibility of the existence of homoatomic centred polyhedra. Indeed, long before the synthesis of $[Rh_{12}Sb(CO)_{27}]^{3-}$ its isoelectronic derivatives $[Rh_{13}(CO)_{24}H_n]^{(5-n)-}$ were obtained.[1] Their structures will be examined in the next Section (in view of their close relationship with the large carbonyl clusters).

Yet another extremely interesting class of polynuclear complexes, constructed in accordance with the eicosahedral motif, is known, namely the gold clusters (Fig.19). The oldest representative of this series, the $[Au_{13}(PMe_2Ph)_{10}Cl_2]^{3+}$ cluster,[32] was initially predicted by Mingos on the basis of EHM calculations.[31] The clusters whose structures have been

investigated so far and whose polyhedra can be represented by an eicosahedron with different numbers of missing vertices are compiled in Table 7 (L is a phosphine ligand). §

Table 7 shows that, in contrast to the gold derivatives examined previously, clusters of this type exhibit a definite tendency towards the retention of the magic number N_{sk} = 18, which is inconsistent with the number N_{sk} = 26 required for the eicosahedron according to the $2n + 2$ rule. For $[Au_8PPh_3)_8]^{2+}$, this is achieved by virtue of the weak coordination of one of the Ph_3P ligands to the central Au atom.[136]



a *b* *c* *d*

Figure 19. Centred gold clusters: *a*) $Au_8L_7^{2+}$; *b*) $Au_9L_8^{3+}$; *c*) $Au_{11}L_{10}^{3+}$; *d*) $Au_{13}L_{10}Cl_2^{3+}$.

On the basis of the preferential contribution of the interaction between the central and peripheral Au atoms to the bonding in the given cluster (this has been established both by calculations[131] and experimentally[139]), one can assume that the magic number N_{sk} = 18 characterises the tendency of the electron shell of the central Au atom in compounds of this type to assume the inert gas configuration.

Table 7. Centred gold clusters based on the eicosahedron.*

Formula	n_{miss}	N_{val}	N_{sk}	Refs.
$[Au_8L_7]^{2+}$	5	100	16	[136]
$[Au_8L_8]^{2+}$	5	102	18	[136]
$[Au_9L_8]^{3+}$	4	112	16	[137]
$[Au_{11}L_{10}]^{3+}$	2	138	18	[138]
$[Au_{13}L_{10}Cl_2]^{3+}$	0	162	18	[32]

*n_{miss} is the number of missing vertices.

In contrast to the mononuclear Au complexes, where a linear configuration and a 14-electron shell are characteristic of many of such compounds, the peripheral Au atoms in the clusters listed in Table 7 occupy fairly uniformly the coordination shell of the central atom, which apparently constitutes a condition for the fulfilment of the EAN rule in mononuclear transition metal complexes. This makes it possible to expect the existence of the clusters, not as yet obtained, $[Au_{10}L_9]^{2+}$ and $[Au_{12}L_{11}]^{4+}$ (or their isoelectronic derivatives involving the substitution of some of the phosphine ligands by halide ligands, which reduces the overall positive charge) and possibly cations of the type $[Au_{14}L_{11}X_2]^{4+}$ or $[Au_{14}L_{10}X_3]^{3+}$ (where X = halogen) with an 18-electron configuration of the central Au atom in all such hypothetical structures. In the case of the 16-electron clusters $Au_9L_8^{3+}$ the somewhat more open flattened Au_9 skeleton (Fig. 19b) is apparently capable of rearranging to a structure with a centred crown.[140]

§A preliminary communication[149] concerning the synthesis and structural study of the mixed $[(Ph_3P)_{12}Au_{13}Ag_{12}(\mu\text{-}Cl_6]^{m+}$ cluster, constructed from three interpenetrating eicosahedra and containing three intrapolyhedral Au atoms, has been published.

5. Lattice Clusters

Here we denote by this term polynuclear transition metal anions, predominantly those of Rh and Pt, where the M_n polyhedron actually represent a fragment of the crystal lattice of the metal. Clusters of the type $[Os_{10}C(CO)_{24}]^{2-}$ or $[Pd_6Fe_6(CO)_{24}H]^{3-}$ (Table 6), which have already been examined, may be assumed to contain layers of metal atoms, with hexagonal close packing, but it is still possible to interpret their electronic structure rationally in terms of a model of the reference octahedron with electron delocalisation over which caps with localised bonds have been constructed. In contrast to this, the examples of large clusters with carbonyl ligands listed in Table 8 cannot be arranged systematically on the basis of the $2n + 2$ rule and even less so the EAN rule. For some of these, the real numbers of valence electrons can be found by means of the CVMO scheme, but, generally speaking, precisely in this class of polynuclear compounds the above scheme starts to become inadequate for the task formulated (see Section II). Comparison of the theoretical magic numbers of valence electrons with the numbers for specific structures is complicated in this instance also by the difficulty of detecting carbonyl (and even more so hydride) ligands in the X-ray diffraction study of large clusters owing to the high scattering capacity of the metal atoms and the intense absorption, as a result of which, for example, the number of CO ligands in the last cluster in Table 8, namely $[Pt_{38}(CO)_{44}]^{2-}$, was established only tentatively

Table 8. Certain Rh and Pt lattice clusters.

Formula	n_{int}	n_{cap}	n_o	N_{val}	N_{sk}	$N^{sk}_{(2n+2)}$	N^{val}_{CVMO}	Refs.
$[Rh_{13}H_3(CO)_{24}]^{2-}$	1	0	6	170	26	38	170	[141]
$[Rh_{14}H(CO)_{25}]^{3-}$	1	1	5	180	24	38	182	[142]
$[Rh_{15}(CO)_{27}]^{3-}$	1	2	4	192	24	38	194	[143]
$[Rh_{15}(CO)_{30}]^{3-}$	1	2	4	198	30	38	—	[144]
$[Rh_{17}(CO)_{30}]^{3-}$	1	4	2	216	24	38	—	[145]
$[Rh_{22}(CO)_{37}]^{4-}$	1	6+3	0	276	24	38	280	[4]
$[Rh_{22}(CO)_{35}H_x]^{5-}$	2	8	2	$273 + x$	$33 + x$	46	—	[146]
$[Pt_{19}(CO)_{22}]^{4-}$	2	0	10	238	34	56	—	[147]
$[Pt_{26}(CO)_{32}]^{2-}$	3	0	6	326	50	60	—	[4]
$[Pt_{38}(CO)_{44}]^{2-}$	6	0	6	470	86	78	—	[4]

Notation: n_{int} is the number of internal atoms, n_{cp} the number of caps, n_o the number of open faces; for the significance of the remaining notation, see previous tables.

In relation to quantitative theoretical schemes, the lattice clusters in general exhibit fully the tendency already mentioned above for polyhedra of medium dimensions: with increase of the size of the polyhedron, its idealised form, consistent with the $2n + 2$ rule, is found to be capable of undergoing increasing distortions, which do not alter the number of valence (or skeletal) electrons. Accordingly, the

$[Rh_{13}(CO)_{24}H_3]^{2-}$ cluster, which can be obtained from a cubo-octahedron by rotating by 180° one of the triangular faces (to reproduce the so-called "twin of the cubo-octahedron"), is isoelectronic with a *closo*-eicosahedron, despite the presence of six open faces, which formally require additional twelve skeletal electrons.

Analysis of structures with Rh_{14}–Rh_{17} polyhedra (Fig. 20), which arise after the addition of caps to the initial Rh_{13} cluster, shows that in the case of large carbonyl clusters there is in essence no difference between the triangular and non-triangular faces as regards the influence on the number of skeletal electrons of the polyhedron. However, these numbers are not predicted by any of the existing theoretical schemes and can apparently be different for polyhedra of isotypical structure. Thus a satisfactory theoretical scheme for large transition metal clusters with carbonyl ligands has not as yet been developed.¶

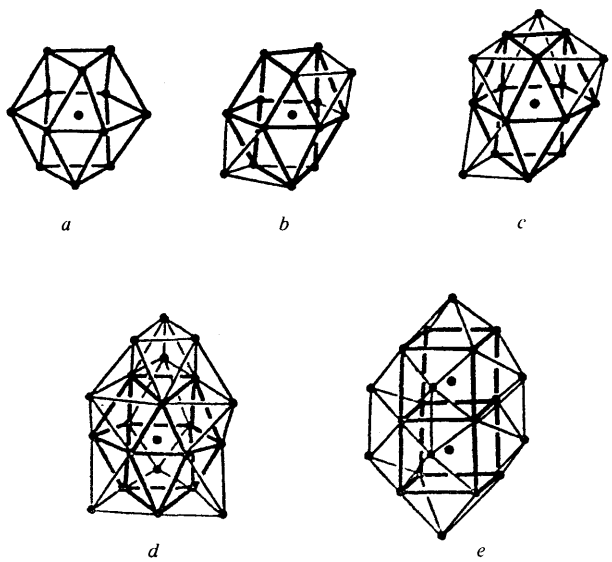


Figure 20. Examples of the structures of large metal clusters (the reference centred polyhedron is indicated): *a*) $[Rh_{13}.H_3(CO)_{24}]^{2-}$; *b*) $[Rh_{15}(CO)_{27}]^{3-}$; *c*) $[Rh_{17}(CO)_{30}]^{3-}$; *d*) $[Rh_{22}(CO)_{37}]^{4-}$; *e*) $[Rh_{22}(CO)_{35}H_x]^{5-}$.

- - - o 0 o - - -

On the basis of the structures of transition metal clusters examined above, it is possible to outline the limits of applicability of the existing schemes for the evaluation of the number of electrons in polyhedra. It follows from the examples in Section II that the "ordered region" in polynuclear transition metal complexes occurs in general in the vicinity of elements in the middle of transition series (Group VI–VIII metals), for "soft" ligands (in the first place CO), and for relatively simple M_n polyhedra with the number of vertices n in the range from 3 to 12. The $2n + 2$ rule or the EAN rule closely related to it (representing the special case for clusters with vertices of order ≤ 3 in which localised bonds can exist) yields the best results for such clusters.

The application of the $2n + 2$ scheme to octahedral metal clusters appears to be the most correct; an increase in the dimensions of the metallopolyhedron leads to increasing deviations of the structures of the clusters from the Wade structures and the corresponding magic numbers (somewhat in contrast to carbaborane derivatives, where eicosahedral clusters approximate most closely to the Wade structures).

The empirical-computational CVMO scheme which in general reproduces satisfactorily the numbers of valence electrons in clusters in the region of applicability of the $2n + 2$ rule, provides a somewhat better description of the electronic structure of clusters of medium dimensions, which sometimes deviates from this rule, and extends a little further into the region of large clusters; however, for a series of Wade polyhedra, this scheme can predict magic numbers which are incorrect. The search for general regularities outside the limits of the range of compounds indicated above and differentiated empirically has not so far achieved notable advances. Because of this, the hypothesis that clusters whose atomic and geometrical structures are governed by the $2n + 2$ rule contain a special type of chemical bond, which is absent from other clusters and which is taken into account explicitly or implicitly by electron counting schemes, appears to be fairly logical. According to all the theoretical and experimental studies, the chemical bond of this type in Wade clusters (and only in such clusters) makes it possible to differentiate independent topologically different exopolyhedral, surface, and intrapolyhedral electron systems with full localisation of electrons in the last two systems, which constitute overall the skeletal system of linkages in the clusters.[40] Thus Wade clusters (and only such clusters) apparently possess a closed configuration with skeletal delocalisation of the electron system, i.e. have the property of "three-dimensional" superaromaticity, which is nowadays attributed, not always with prejustification, to any polyhedral molecule.

In the superaromatic molecules, the bonding intrapolyhedral electron system ensures the stability of the cluster skeleton and the surface system ensures the electron delocalisation. The manifestation of superaromaticity in real cluster complexes, like the manifestation of the usual aromaticity in cyclic organic molecules, requires the fulfilment of specific geometrical conditions, which apparently follow from the requirement for the overlap of orbitals in the intrapolyhedral electron system. An increase in the size of the inner cavity, the appearance of open faces, or the introduction of atoms of post-transition elements into the polyhedral skeleton lead to a gradual loss of the property of superaromaticity and a transition to structures of clusters which do not obey the $2n + 2$ rule.

Comparison of structural data with theoretical predictions thus makes it possible to differentiate among the set of polynuclear compounds the region of clusters for which the model of chemical bonding in a superaromatic three-dimensional system developed at the present time is valid. However, at the present level of chemical theory, the model itself is mainly empirical in character and has not been rigorously justified mathematically. The search for such mathematical justification should apparently be prosecuted in the field of topology;

¶A dependence of the type of packing of the atoms in the metallopolyhedron on the average number of valence electrons per intrapolyhedral metal atom has been proposed recently for clusters of this type on the basis of a modified Hume–Rothery rule.[150] The total numbers of valence electrons in the clusters investigated, calculated on the basis of idealised types of packing, agree with the real numbers to within 4% (the discrepancies are in the range from 0 to 13 valence electrons).

the results of such investigations (should they be successful) might introduce a significant modification into the theoretical apparatus of the chemistry of cluster compounds.

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The Electronic Structure of Transition Metal Cluster Complexes with Weak- and Strong-field Ligands

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A systematic account and a survey of the results of quantum-chemical and spectroscopic studies of the electronic structure of transition metal cluster complexes are presented. In terms of the theory of canonical molecular orbitals and the theory of weak- and strong-field ligands, the concept of the structure and stability of the clusters taking into account the influence of the ligands and transition metal atoms on the characteristics of the M-M bonds has been formulated. The characteristic features of the delocalisation of the valence electrons of the M atoms in the M_n groups, the intercluster interaction, the density of the M atoms in the clusters, and the effects of cluster formation in the optical and X-ray spectra are discussed.
The bibliography includes 137 references.

CONTENTS

I. Introduction 344
II. The electronic structure of chloride and carbonyl clusters 344
III. Distribution of clusters in the periodic system 347
IV. The influence of the type of ligands on the structure of clusters 348
V. The effects of cluster formation 352
VI. The spectroscopy of cluster complexes 353
VII. The nature of the M-M bonds in the chloride clusters of 4*d* and 5*d* elements 357

I. INTRODUCTION

In the modern chemistry and physics of clusters, one of the main taks is to create a general theoretical conept concerning the structure and stability of clusters whereby one can account for the existence of these complexes and formulate the principles governing their structure as a function of the position of the transition metal in the Periodic System, the formal valence of the M atoms, and the individual nature of the ligands; such a concept would constitute a general solution of the problem of the mutual influence of the nature of the transition metal and the ligands on the stability of cluster structures. The knowledge of the electronic structure of the clusters is undoubtedly a basis for the understanding of their structure, stability, and reactivity. The electronic structure of transition metal cluster complexes has been the subject of numerous theoretical studies in the last twenty years. The present review is devoted to the discussion of the results of these investigations and also the results of experimental studies of the spectroscopic properties of cluster compounds which supplement and refine the quantum-chemical calculations of the electronic structure.

II. THE ELECTRONIC STRUCTURE OF CHLORIDE AND CARBONYL CLUSTERS

Non-empirical and semi-empirical methods of the theory of delocalised molecular orbitals,[1-6] the electron gas method,[7] topological methods,[8,9] and the ligand field theory[10] are used in the quantum chemical calculations of the electronic structures of isolated cluster complexes. The references quoted above refer to review papers which have been published during the last decade. The results of spectroscopic and theoretical studies of the nature of the M-M bonds in transition metal cluster complexes (with the exception of dinuclear complexes) with strong M-M interactions are described in a recent review.[11]

The cluster chlorides and carbonyls of transition metals have been investigated most fully both experimentally and theoretically at the present time; attention is in fact concentrated on these substances in the present review. Weak π-donors (Cl atoms) and strong π-acceptors (CO molecules) occupy positions at the opposite ends of the general series of ligands and the study of clusters incorporating precisely these ligands is therefore most fruitful for the solution of the problems mentioned above in the most general form.

Table 1. Electronic structure parameters of clusters.

Cluster	Symmetry	R_{M-M}, Å	B_{M-M}	Bonding "M-M" MO	N_{M-M}	n_{M-M}	P_{M-M}	Refs.
$Mo_2Cl_8^{4-}$	D_{4h}	2.14	1	$a_{1g}eb_{2g}$	8	8	$4(\sigma+2\pi+\delta)$	[1,6,14]
$W_2Cl_9^{3-}$	D_{3h}	2.41	1	$a_1'e'$	6	6	$3(\sigma+2\pi)$	[2-4]
$Re_3Cl_{12}^{3-}$	D_{3h}	2.47	3	$a_1'a_2''e'e''$	12	4	$2(\sigma+\pi)$	[2-4]
$Nb_6Cl_{18}^{6-}$	C_{2h}	2.86	5	$a_ua_gb_ua_gb_g$	10	2	$1(\sigma)$	[2]
$Mo_5Cl_8^{3+}$	C_{4v}	2.58	8	$a_1a_1a_1ab_1eeb_2e$	19	2.4	$1.2(\sigma+[\pi])$	[4]
$Ta_6Cl_{12}^{3+}$	O_h	2.93	12	$a_{1g}t_{1u}t_{2g}a_{2u}$	15	1.2	$0.6(\sigma)$	[2,19]
$Re_2(CO)_{10}$	D_{4d}	3.02	1	a_1	2	2	$1(\sigma)$	[2-4]
$Os_3(CO)_{12}$	D_{3h}	2.88	1	$a_1'e'$	6	2	$1(\sigma)$	[2-4,11]
$Ir_4(CO)_{12}$	T_d	2.68	1	a_1el_2	12	2	$1(\sigma)$	[2-4,11]
$Mo_2(O_2CR)_4$	D_{4h}	2.11	1	$a_{1g}e_ub_{2g}$	8	8	$4(\sigma)$	[6,15]
$Ru_2(O_2CR)_4^+$	D_{4h}	2.28	1	$a_{1g}e_u$	6	6	$3(\sigma+2\pi)$	[4,17]
$Mo_3O_{13}^{14-}$	C_{3v}	2.52	3	a_1e	6	2	$1(\sigma)$	[4]
$Ru_3O_{12}^{12-}$	C_{3v}	2.55	2	a_1ee	8	4	$2(\sigma+\pi)$	[4]

Notation: R_{M-M} is the M-M distance, B_{M-M} the number of two-centre M-M bonds, N_{M-M} the total number of valence electrons in the M-M bonds, n_{M-M} the number of valence electrons per two-centre M-M bond, and P_{M-M} the multiplicity of the two-centre M-M bond.

The results of semi-empirical[1-6,11-15] and non-empirical[16-19] molecular-orbital calculations (some examples are presented in Table 1) revealed the most important features of the electronic structures of the chloride and carbonyl clusters and the fundamental differences between clusters containing ligands of different types.

In the chloride clusters the energy splitting of the valence *d* orbitals of the M atoms in the mononuclear fragment in the field of weak π-donor ligands (Cl atoms) is slight and much less pronounced than the corresponding splitting of these atomic orbitals (AO) following the appearance of M-M bonds, i.e. on formation of the cluster (Fig.1).

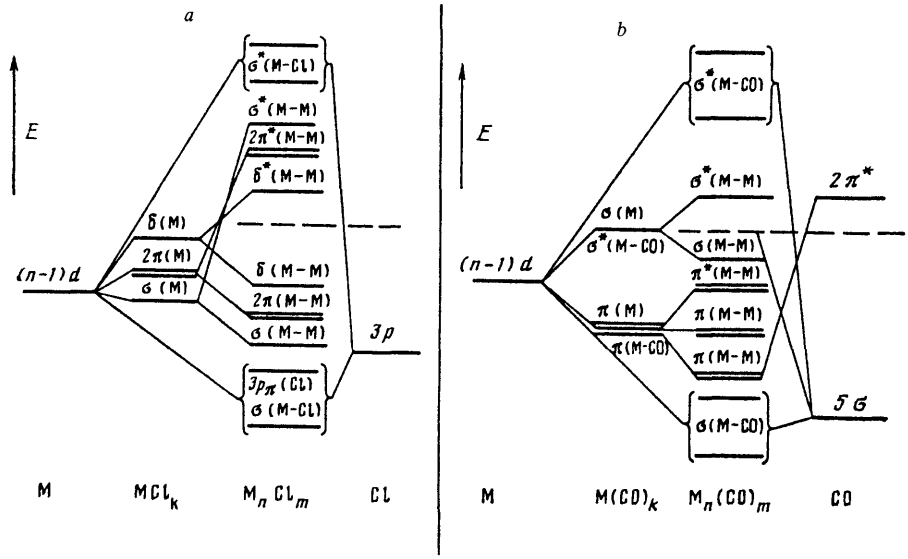

Figure 1. The molecular orbitals in the chloride and carbonyl clusters; the MO populated by electrons and the unoccupied MO are shown below and above the dashed lines respectively.[4]

The bonding and antibonding and sometimes also non-bonding molecular σ, π, and δ orbitals of the M–M bonds arise in the electronic structure of the chloride cluster under these conditions. The number and symmetry of these MO are rigorously individual for each chloride cluster, are determined by its stereochemistry, and are the most important characteristic of its electronic structure.[1,4]

A different picture is observed in the electronic structure of carbonyl clusters: the energy splitting of the valence *d* orbitals of the M atoms of the mononuclear fragment in the field of strong π-acceptor ligands (CO groups) is pronounced and greatly exceeds their energy splitting induced by the formation of the M–M bonds when the cluster is produced (Fig. 1).[4,20,21]

This, the first important difference between the electronic structures of the chloride and carbonyl clusters, is caused by the fact that in the carbonyl clusters the two-centre M–L bonds are characterised by an enhanced multiplicity (M ← CO donor–acceptor σ interactions and M → CO dative π interactions) owing to the strong π-acceptor character of the CO groups, in contrast to the chloride clusters, where the two-centre M–L interactions represent virtually single two-electron bonds predominantly of the covalent σ-type. As a result of the different types of behaviour of the valence *d* orbitals of the M atoms in the fields of different ligands, the following situation arises: in the electronic structure of the chloride cluster, the molecular orbitals which are occupied by electrons and are responsible for the M–M interactions always constitute a single (and fairly isolated as regards energy) group, which incorporates in the general case σ, π_1, π_2, and δ MO (with increase of the number of valence *d* orbitals of the M atoms involved in the bonding with the Cl atoms and with the increase of the coordination number of each M atom in the cluster, initially the δ compound and then the π_1 and π_2 components are successively eliminated from the M–M interactions and only the σ component remains). In the vast majority of the known systems only the bonding molecular orbitals associated with the σ, π_1, π_2, or δ M–M interactions are occupied by electrons, while the corresponding antibonding MO are populated by only one–two electrons and in only rare instances.[1–4] On the other hand, in the electronic structure of the carbonyl cluster the electron-occupied MO of the M–M interactions are always clearly subdivided into two groups, which are not interconvertible in terms of energy: the first includes all the bonding and antibonding π molecular orbitals, while the second includes the bonding σ molecular orbitals of the M–M interactions. The electronic energies of the MO of the first group are appreciably reduced because these MO are simultaneously solely bonding orbitals in relation to the dative M → CO π-bonds; the electronic energies of the MO of the second group are greatly increased because they are simultaneously solely antibonding orbitals in relation to the M–CO σ-bonds. Insofar as all the molecular orbitals which are bonding in relation to the dative M → CO π-bonds and hence all the bonding and antibonding MO of the M–M π-bonds are fully populated by electrons in the electronic structure of the carbonyl cluster, only the highest (in terms of energy) occupied MO of the M–M σ-bonds are responsible for the M–M interactions in the carbonyl cluster.[4,20,21]

The above characteristics features of the electronic structure of the carbonyl clusters are the reason why the bonding and antibonding contributions to the M–M π-bonding approximately cancel out, while the π-contribution to the energy of the M–M interactions is either altogether absent or is slightly antibonding, the π-electron density being concentrated in the region of the M–CO bonds and mainly only single M–M σ-bonds, characterised by comparatively large internuclear distances and a reduced strength, are formed. The solution of the variational problem for the $Re_2(CO)_{10}$ cluster[22] showed that the decrease of the overall M–M bond energy is almost wholly responsible for the increase of the total energy of the cluster with decrease of the M–M distance below the equilibrium value of 3.02 Å; the decrease of the overall M–M bond energy is caused in its turn by the π-antibonding effects, by the energy destabilisation of the carbonyl cluster owing to the M–M π-interactions.

The electronic structure of the chloride clusters presupposes the bonding character of not only the σ- but also frequently the π- and even δ-interactions of the M–M type. For this reason, the multiplicity of the two-centre M–M bonds in such clusters varies within wide limits, reaching the limiting unique value $4(\sigma + 2\pi + \delta)$ for the M–M bonds in the $Re_2Cl_8^{2-}$, $Tc_2Cl_8^{3-}$, $Mo_2Cl_8^{4-}$, and similar dinuclear clusters. In the chloride clusters the multiple two-centre M–M bonds arise whenever this is allowed by the stereochemistry of the cluster group and the effective number of electrons involved in the M–M interactions. This is why the energies of the two-centre M–M bonds and the M–M distances in the chloride clusters vary within wide limits, ranging from weak interactions and long bonds in certain hexanuclear clusters to very strong interactions and extremely short bonds in the dinuclear groups.[23,24]

Thus M–M bonds with very high multiplicities and energies and sharply reduced M–M distances are formed only in the chloride clusters: such two-centre bonds involve σ-interactions, frequently π_1- and π_2-interactions, and sometimes even δ-interactions, whose electron densities concentrated in the region of the M–M bond hardly affect the ligands. The high stability of the chloride clusters of the formally low-valence 4*d* and 5*d* elements (Nb, Ta, Mo, W, Tc, Re), determined by the high M–M bond energies, is accompanied by the instability of the corresponding mononuclear anions ($TaCl_6^{4-}$, $MoCl_6^{4-}$, WCl_6^{3-}, $ReCl_6^{3-}$), which agrees with experimental findings.[25]

The second important difference between the electronic structures of the chloride and carbonyl clusters concerns the character of the M–M bonds. In the chloride clusters the main contribution to the MO of the M–M bond and to the overall orders of these bonds comes solely from the valence $(n-1)d$ orbitals of the M atoms and the bonds between the metal atoms are formed in the interaction of virtually only the $(n-1)d$ electrons of the M atoms.[1–4,26] In the carbonyl cluster also the valence *ns* and particularly *np* orbitals of the M atoms make a significant contribution together with the $(n-1)d$ orbitals, sometimes even the dominant contribution, to the σ-bonding M–M molecular orbitals and to the overall orders of the M–M σ-bonds.[21] This difference between the electronic structures is probably caused by the fact that in the chloride clusters the M atoms supply the *ns* and *np* electrons for the formation of bonds with ligands, such electrons being most suitable for this purpose in terms of symmetry and energy, while most of the $(n-1)d$ electrons are retained for the formation of various M–M bonds. On the other hand, owing to the high π-acceptor capacity of the ligands, in the carbonyl clusters a considerable proportion of the valence $(n-1)d$ electron density, which is more suitable as regards symmetry and energy than the *ns* and *np* states of the M atoms, is involved in the dative M → CO π-bonds; as a result of the formation of direct M–M σ-bonds, the number of the remaining $(n-1)d$ electrons is clearly insufficient and the use of the valence *ns* and particularly *np* electrons of the M atoms is necessary. The increased *np* character of the molecular orbitals of the M–M σ-bonds in the carbonyl clusters also entails (together with the antibonding character of these MO in relation to the donor–acceptor M–CO σ-bonds already mentioned), an increase of the energies of these MO, which accounts for the appreciably reduced energy of the two-electron two-centre M–M bonds in the cluster carbonyls compared with the cluster chlorides.[3,21]

This second difference is significant in the chemistry of cluster compounds in yet another respect. It is actually the decisive cause of the situation where 3*d* elements form cluster carbonyls but not cluster chlorides. In particular, the formation of the M–M bond in $Mn_2(CO)_{10}$ (i.e. the formation of a cluster) is associated with the involvement in this σ-bond of the valence 4*s* and 4*p* electrons of the Mn atoms not participating in the dative π-bonding with the ligands; on the other hand the participation of all the 4*s* and 4*p* electrons of the Cl atoms in the bonds with the ligand in $Cr_2Cl_9^{3-}$ explains the absence of any kind of M–M bond in this anion (i.e. the absence of a cluster), because, owing to the spatial contraction of their charge clouds, the valence 3*d* electrons of the M atoms cannot alone ensure the formation of any kind of strong M–M bond over the long M–M distances characteristic of both $Mn_2(CO)_{10}$ and $Cr_2Cl_9^{2-}$ (2.92 and 3.21 Å).[22,27]

The third difference lies in the fact that in the chloride clusters the molecular orbitals of the M–M bonds are of the purely "metallic" character and the contribution of the valence orbitals of the ligands to them is small; on the other hand, in the carbonyl clusters this contribution is appreciable. An important feature of the electronic structure of the chloride cluster is as follows: in the unique MO system of the cluster, the molecular orbitals responsible for the M–M interactions always constitute a distinct and isolated, in terms of energy and character, group and are predominantly of the $(n-1)d$ electron type: the isolation of these molecular orbitals is independent of either the energy and steric characteristics of the valence orbitals of the M atoms (i.e. of the nature of the transition element) or of the symmetry of the cluster group, which means that the M–M and M–L electronic interactions in the chloride clusters are to a large extent isolated from one another and their mutual influence is very weak, while the properties of the M–M and M–L bonds (in the first place their energies) are additive; in the cluster carbonyls everything is completely different and the characteristics of their M–M and M–L bonds are non-additive.

The isolation of the electronic M–M and M–L interactions in the chloride clusters makes it possible to solve the problem of their stability in a generalised form. The molecular orbitals of the M_n groups, which constitute the "metallic nuclei" of all the known chloride clusters of the 4*d* and 5*d* elements, have been calculated[2,28–30] (the symmetry of the point group of the cluster is indicated in brackets): M_2 for $M_2X_8(D_{4h})$, M_2 for $M_2X_9(D_{3h})$, M_2 for $M_2X_8(C_{2v})$, M_2 for M_3X_9 or $M_3X_{12}(D_{3h})$, M_2 for $M_3X_{12}(C_{3v})$, M_4 for $M_4X_{16}(C_{2h})$, M_4 for $M_4X_{16}(T_d)$, M_6 for M_6X_8 or $M_6X_{14}(O_h)$, and M_6 for M_6X_{12} or $M_6X_{18}(O_h)$. The electronic interactions arising in typical cases within the limits of each M_n group (direct M–N bonds) are represented by a characteristic set of bonding, non-bonding, and antibonding MO. These are in fact the molecular orbitals of the M–M bonds in the unique electronic structure of the M_nX_m chloride cluster as a whole. The number and character of such MO are determined not only by the number of M atoms in the M_n group but also by the number of ligands and the symmetry of their arrangement in the corresponding cluster group, i.e. by the detailed stereochemistry of the entire M_nX_m chloride cluster.[2,4,28,29]

There exist also chloride clusters, where, among the molecular orbitals responsible for the M–M interactions, only the bonding MO are populated (as a rule completely) by electrons (not involved in the M–L bonds), while the corresponding antibonding MO are unoccupied or in rare instances are populated by 1–2 electrons.[10] The stability of the M_nX_m chloride cluster as a whole and of its M_n group separately should therefore be attributed precisely to this (optimum) electron population of the molecular orbitals of the direct M–M bonds. The characteristic number of electrons ensuring the maximum stability of the M_n group when M–M bonds arise in it as a consequence of the complete population of all its bonding MO (and only the bonding MO) by electrons can be determined for each M_n group.

Thus it is possible to outline the limits of stability of each M_nX_m cluster taking into account its characteristic number of electrons and the individuality of the *d* element (the total number of valence electrons of the M atom) and its formal valence (the number of valence electrons of the M atom in the M–L bonds). Namely, by sorting through the transition metals of various Groups in the Periodic System, i.e. by scanning the number of valence electrons in their atoms, it is possible to outline the range of 4*d* and 5*d* elements (and at the same time indicate their formal valences), which can form stable chloride clusters.[4] It is then found that the clusters can be stable only in structures of the lowest chlorides of heavy Group V, VI, and VII *d* elements, since the total number of valence electrons in their atoms is such that it enables them to ensure the stability of one or (more frequently) several forms of clusters for a low oxidation state. On the other hand, the number of valence electrons in Group III and IV *d* elements is too small and that of the electrons of the M atoms (for any realistic oxidation states of the metal), not involved in the formation of bonds with the ligands, is clearly insufficient to populate the bonding orbitals of the M–M bonds in the M_n cluster of any form and hence for the formation of a more or less stable chloride cluster. In the atoms of Group VIII 4*d* and 5*d* elements the number of valence electrons is too large, which leads to the population by the electrons not involved in the M–L bonds not only of the bonding but also of the antibonding molecular orbitals of the M–M bonds in a cluster of any form and hence to a decisive destabilisation of the structure (and the absence of any cluster); for a low formal valence of M, whereupon a large number of the valence electrons of the M atoms are involved in the M–L bonds and whereupon a seemingly optimum number of electrons remains available for the formation of the M–M bonds, the possibility of the formation of such bonds and of the M_n cluster is sharply limited (owing to the large number of bonds of each M atom with the ligands) by purely steric factors.

The results of calculations of the molecular orbitals of both the M_n groups[2,28–30] and the M_nX_m cluster groups as a whole[2,3,11] indicate, firstly, the criteria of the stability of one or several forms of chloride clusters for a given formal valence of a specific *d* element. These results show that both dinuclear and trinuclear but not hexanuclear chloride clusters should be stable for Tc and Re; the dinuclear cluster should be relatively unstable for Nb and Ta and octahedral clusters should be most characteristic; almost all the known forms of cluster groups should be stable for Mo and W in different oxidation states (2–4). The above approach possesses predictive power in relation to almost all *d* elements.

Secondly, these results explain the stability of the integral oxidation states of some *d* elements ($MoCl$–Mo_6Cl_{12}, WCl_3–W_6Cl_{18}, $ReCl_3$–Re_3Cl_9, etc.) and the non-integral oxidation states of others ($NbCl_{2.33}$–Nb_6Cl_{14}, $NbCl_{2.67}$–Nb_3Cl_8, $TaCl_{2.50}$–Ta_6Cl_{15}, etc.), i.e. the causes of the non-stoichiometry of their lowest chlorides; in the presence of six (Mo, W) or seven (Tc, Re) valence electrons in the M atom, the maximum stability of particular chloride clusters is attained for an integral electronic configuration of the M atom (d^2, d^3), i.e. for an integral formal valence of the metal M characterising the number of its valence electrons in the bonds with the ligands. When five (Nb, Ta) valence electrons are present in the M atom, the cluster groups with a non-integral (between d^2 and d^3) electronic configuration of the M atoms are mainly stable, which accounts for their fractional formal valence in the corresponding non-stoichiometric chlorides.

Thirdly, the results of calculations reveal and explain the unique ability of the heavy Group VI *d* elements to produce the greatest number of stable clusters among almost all the known forms. It was found that all the oxidation states (2, 3, and 4) potentially suitable for cluster formation are thermodynamically stable for molybdenum and tungsten, because in these oxidation states the Mo and W atoms have the electronic configurations (d^4, d^3, d^2), which are most suitable in the sense that the number of valence *d* electrons in each M atom capable of participation in the M–M bonds ensures the stability of at least one or even several different forms of clusters by populating only the bonding (but not antibonding) M–M molecular orbitals.

These results made it possible to establish a distinct relationship between the stable form of the chloride cluster (and its stability in general), the formal valence of the transition metal, and its position in the Periodic System, and, finally, to explain why chloride clusters are stable in the main only for the heavy Group V, VI, and VII transition elements (Nb, Ta, Mo, W, Tc, Re) and are as a rule unstable for the Group III, IV, and VIII elements (La, Hf, Os, Ar, Pd, and their analogues).[3,4]

The characteristics of the electronic structure of the carbonyl clusters revealed by the calculation show that each M atom supplies (regardless of the stereochemistry of the cluster and its component mononuclear fragments) exactly six valence electrons for the formation of the necessary (for the existence of the carbonyl cluster) dative M–CO π-bonds. The molecular orbitals (bonding in relation to the dative M–CO π-interactions) occupied by these electrons are at the same time both bonding and antibonding in relation to the M–M π-interactions. The valence electrons of the M atoms involved in the dative M–CO π-bonds are therefore as a whole "frozen" in the M–L bonds and do not participate in M–M bonds. This is precisely the reason why the carbonyl clusters are stable only for those transition metals in the atoms of which the number of valence electrons is greater than six (i.e. at least seven). Only then do the σ-bonding M–M molecular orbitals which have higher energies and are responsible for the formation of the M–M bonds in the carbonyl clusters, become populated with electrons. This accounts for the known fact that the cluster carbonyls are formed mainly only by Group VII (Mn, Tc, Re) and particularly VIII (Fe, Co, Ru, Rh, Os, Ir) transition metals and are unstable for the metals in the first half of the transition series.[10]

It is of interest that hitherto no clusters have been found where each M atom would supply exactly six of its valence electrons for the formation of the M–M bond. On the one hand, these can be caused by the special stability of the spin-paired d^6 electronic configuration[31–33] and, on the other hand, it follows directly from the considerations described above: six electrons are too many for the formation of an energetically stable cluster with π-donor ligands (Cl) but are too few to ensure the occupation of the σ-bonding M–M molecular orbitals in the cluster with π-acceptor ligands (CO) and hence to impart energy stability to the latter.

III. DISTRIBUTION OF CLUSTERS IN THE PERIODIC SYSTEM

The isolated nature of the M–M and M–L interactions in the chloride clusters and, in contrast, the strong mutual influence of these interactions in the carbonyl clusters permit the conclusion that the main features of the clusters with π-donor ligands should be almost independent of the individual characteristics of ligands of this type and should remain almost unchanged on passing from one π-donor ligand to another. On the other hand, clusters with π-acceptor

ligands should be extremely sensitive to the individual characteristics of ligands of this type and their structure should change significantly on replacing one π-acceptor ligand by another.[4]

The available experimental facts confirm these ideas or at least do not conflict with them.[31-42] Indeed clusters with many different π-donor ligands have properties which are similar in broad outline (the replacement of these ligands does not influence greatly the structure and stability of the cluster) although there are no sufficient grounds for a fully unified approach to these clusters. On the other hand, the replacement of π-acceptor ligands leads to significant changes in the structure and stability of the clusters; one of the causes of this is probably that the π-acceptor ligands ensure to some extent the delocalisation of the valence electrons of the M atoms on formation of the dative M–L π-bonds as a function of the individual properties. Thus, in contrast to Tc, Re, Ru, Rh, Os, and Ir, "pure" carbonyl clusters are unknown for Pd and Pt, whose atoms have the maximum number (ten) of valence electrons, but instead either the molecular dinuclear cations of the type $[Pd_2(CO)_2]^{q+}$, with a reduced (owing to the ionisation of the complex) effective number of valence electrons in the M atoms[44] or the dinuclear compounds $Pd_2(PPh_3)_4(NO)_2$ and $Pt_2(PPh_3)_4(NO)_2$, where the ligands are NO molecules with π-acceptor properties even more pronounced than those of the CO groups, are stable.[44] New features in the electronic structure of M–M bonds can be observed in cluster groups with PR_3 ligands: $Ru_2(\mu\text{-}PPh_2)_2.(NO)_2$, $Rh(PPh_3)_4(CO)_2$, $Rh_2Cl_2(PF_3)_4$, $Ir_2Cl_2(PF_3)_4$, $Rh_2(PF_3)_8$, $Ir_2(PF_3)_8$, etc. Such compounds are known hitherto only for some of the elements of the platinum group.[45-50]

Thus the main conclusion which follows from the results of the study of the electronic structure of the clusters of *d* elements can be formulated thus: the M–M interactions in the clusters are determined not only by the nature of the *d* element but also depend significantly on the nature of the ligands, because the electronic structure of different M–L bonds has by no means the same influence on the electronic structure of the M–M bonds. In clusters with ligands of the first type fundamental differences are observed in the stereochemistry, energy, and multiplicity of the M–M bonds, in the stability of the clusters as a function of the position of the transition metal in the Periodic System, etc. However, one should note that, together with the natural similarity of the properties of the isoelectronic clusters within the limits of any one variety (for example, the 40-electron $MO_6Cl_8^{4+}$ and $Nb_6Cl_{12}^{2+}$ clusters or the 8-electron MO_2 cluster from $Mo_2Cl_8^{4-}$ and the Re_2 cluster from $Re_2Cl_8^{2-}$), there is evidence[4] indicating definite signs of similarity in the properties of isoelectronic clusters belonging to different categories [for example, the 72-electron $Mo_2Cl_8^{4-}$ and $Mo_2(O_2CR)_4$ clusters, the 108-electron $Re_2Cl_{12}^{3-}$ and $Ru_3O_{12}^{2-}$ clusters, or the 18-electron W_6 cluster from W_6Cl_{18} and the Rh_6 cluster from $Rh_6(CO)_{16}$]. This must be taken into account to avoid overestimating the differences between the structures of the chloride, carbonyl oxygen, carboxylate, and other clusters of 4*d* and 5*d* elements.

The mutual influence of the metal atoms and the ligands in the clusters is manifested mainly by the fact that a specific region in which the cluster structures of the *d* elements occur in the Periodic System is characteristic of each ligand. The discussion of the influence of the ligands on the character of the M–M interactions in the transition metal clusters and hence on the structure and properties of the clusters is on the whole treated in the present review in the nature of a survey, because the Cl atoms constitute a prototype of a whole series of comparatively weak π-donor ligands, while CO molecules serve as a prototype of a series of active π-acceptor ligands; this general approach helps in securing an answer to the main question: with which transition metals and with what ligands can stable cluster structures be formed?

Ligands of the π-donor type should promote the occurrence of cluster structures in compounds of heavy (4*d*, 5*d*) transition elements only in the first halves of the series for low oxidation states of the metal, whereupon the valence electrons of the M atoms not involved in bonds with the ligands can form strong M–M σ-, π-, and even δ-bonds. The formation of cluster structures in yttrium, lanthanum, zirconium, and hafnium compounds is most difficult because of the small number of valence electrons in their atoms. Cluster structures of π-donor ligands cannot arise in formally low-valence compounds of the remaining 4*d* and 5*d* elements owing to the critically large number of valence electrons in their atoms, which leads to an excess of electrons in the M–M bonds, as a result of which the antibonding M–M orbitals are effectively populated and the bonds between the metal atoms vanish.

Ligands of the π-acceptor type should promote the appearance of cluster structures in compounds of all (3*d*, 4*d*, 5*d*) transition elements only in the second halves of the series, whose atoms have a sufficient number of valence electrons also for the formation of the dative M–L π-bonds necessary to ensure the stability of the compounds and for the formation of M–M bonds. The appearance of cluster structures is most difficult in compounds of the elements of the copper subgroup and especially zinc owing to the supersaturation of their atoms by valence electrons. Cluster structures with π-acceptor ligands cannot appear in compounds of the *d* elements at the beginning of the transition series in connection with the small number of valence electrons in their atoms, which is frequently insufficient even for the formation of strong M–L bonds in the mononuclear complexes. Thus the limits of the stability of the transition metal cluster compounds in the Periodic System can be represented schematically as follows:

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg

π-donor ligands — π-acceptor ligands

An analogous concept concerning the formation and structure of transition metal cluster complexes has been developed within the framework of the ligand field theory.[10]

Thus despite the fact that a detailed explanation of the similarity and differences between all the characteristics of clusters with ligands of different types is so far impossible, one can already achieve a reliable and simple interpretation of the fundamental features of the cluster theory—the question of the stability of clusters as a function of the nature of ligands and also the electronic state of the transition metal atoms and the position of the transition metal in the Periodic System, i.e. the nature of the *d* element.

IV. THE INFLUENCE OF THE TYPE OF LIGANDS ON THE STRUCTURE OF CLUSTERS

The influence of the nature of ligands on the properties of cluster compounds is manifested not only by the fact that the type of ligands (more precisely the character of the M–L bonds) determines in many respects the electronic structure of the M–M bonds and that a specific region of the occurrence of clusters in the Periodic System is characteristic of each type of ligand, but also by the fact that the key properties of some (for example, chloride) clusters are associated with

their "metallic nucleus" (the M_n group), while the properties of others (carboxylate, carbonyl, and oxygen clusters) are in many respects determined by the ligand environment.

Furthermore the character of the interaction of the clusters in crystals of different transition metal compounds is likewise determined in many respects by the nature of the ligands. The clusters differ appreciably in their capacity to enter or not enter into the intercluster interaction: some of these (chloride and related systems) usually remain crystal-chemically isolated in the form of "island complexes", while others (oxygen and similar groups) are involved as a rule in strong intercluster interactions and because of this all the cluster fragments throughout the crystal are drawn together into a kind of "supercluster". This influences the properties of cluster compounds and in the first place structure-sensitive properties such as the X-ray electronic and emission spectra, the chemical shifts of the lines due to the metal in such spectra, the optical electronic and vibrational infrared and Raman spectra, the magnetic properties of the crystal, its conductivity, etc.

1. Non-bridged Dinuclear Chloride Clusters

One of the most striking manifestations of the "non-interference" of the ligand environment in the formation of the electronic structure of the M–M bond is provided by the non-bridged dinuclear M_2L_8 clusters with D_{4h} symmetry (Fig. 2). Such clusters are formed by Group VI and VII 4*d* and 5*d* elements (Mo, W, Tc, Re) with participation of ligands of the type Cl^-, Br^-, I^-, SCN^-, etc.

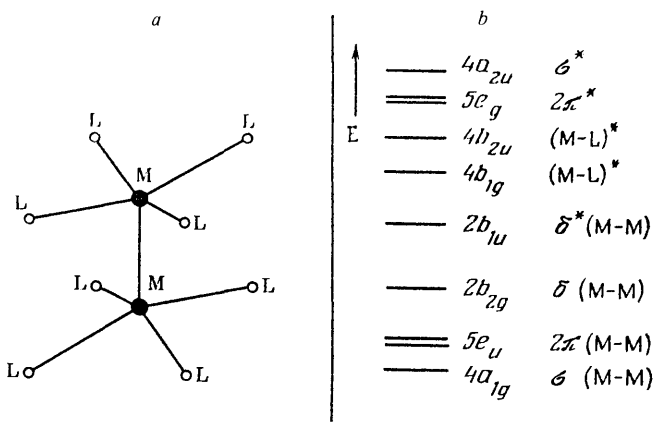

Figure 2. The molecular structure (*a*) and the one-electron energy diagram (*b*) of the highest occupied and lowest unoccupied molecular orbitals of the dinuclear M_2L_8 clusters with D_{4h} symmetry.[17]

The chloride clusters M_2Cl_8 have been most thoroughly investigated.[1,12,14,15,17,30,51–54] The unusual stereochemistry of the M_2Cl_8 clusters (the especially short M–M distance and the eclipsed orientation of the MCl_4 fragments linked to one another directly via an M–M bond without any bridging ligands), their extremely high thermodynamic stability, the specificity of the ligand substitution processes and oxidation-reduction processes, as well as many other properties—all these are factors which are undoubtedly directly related to the characteristics of the electronic structure of the multiple M–M bonds and can be accounted for at the electronic level by the formation of the quadrupole ($\sigma + 2\pi + \delta$) M–M bond.

Thus the two-centre M–M bonds with the maximum possible multiplicity (4) and the highest energy known hitherto among cluster compounds exist in the M_2Cl_8 clusters. Eight valence *d* electrons (four electrons from each M atom) are effectively involved in this strong bond and one (δ) component of this bond limits the mutual rotation of the two MCl_4 fragments about the line of the M–M bonds, i.e. about the rotational fourfold axis of the cluster, promoting thereby a significantly eclipsed (D_{4h}) but not crossed (D_{4d}) conformation of the dinuclear group. Precisely because the energy of the M–M δ-bond is sufficiently high, the M_2Cl_8 (D_{4h}) cluster is not converted into the D_{4d} form where the endo-effect of the interligand repulsion would have been sharply reduced but the M–M δ-bond would have been absent. The barrier to the internal rotation of M_2Cl_8, calculated as the difference between the total energies of the cluster for the eclipsed (D_{4h}) and crossed (D_{4d}) conformations, is close to the energy of the M–M δ-bond[12,30,54] and this result shows yet again that the unusual (D_{4h}) conformation of the M_2Cl_8 cluster arises due to the strong M–M δ-bond without which the observed D_{4h} form of the non-bridged chloride clusters would have been energetically unstable.

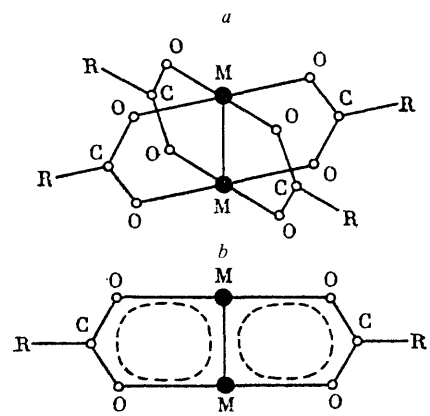

Figure 3. The molecular structure of the dinuclear $M_2(O_2CR)_4$ carboxylate clusters with D_{4h} symmetry (*a*) and the system of delocalised M–M and M–L π-bonds (*b*).[59]

2. Dinuclear Carboxylate Complexes

In contrast to the non-bridged chloride clusters M_2Cl_8, where the electronic structure of the M–M bond plays the main role, the dinuclear carboxylate clusters (clusters with O_2CR ligands) constitute an example of the active involvement of the ligand environment in the formation of the cluster complex as a whole. The $M_2(O_2Cr)_4$ cluster groups, which are characteristic mainly of heavy Group VI, VII, and VIII *d* elements,[55–58] also have the D_{4h} symmetry (Fig. 3), but, in contrast to M_2Cl_8, where the M–L bonds are predominantly of the single σ-character without an appreciable π-contribution and where the involvement of the valence electrons of the ligands in the M–M molecular orbitals is small, in the $M_2(O_2CR)_4$ carboxylate clusters the π-interaction also makes

an appreciable contribution to the M–L bond and the multiplicity of the latter is greater than unity; furthermore, the molecular orbitals of the M–M and M–L bonds do not differ in this instance quite so markedly in their one-electron energies and the contributions of the valence *d* orbitals of the metal atoms.

Compared with M_2Cl_8, the role of the ligands in the formation of M–M bonds in $M_2(O_2CR)_4$ is appreciably enhanced, particularly as regards the M–M π_1- and π_2-interactions.[15,59] In the $M_2(O_2CR)_4$ cluster the energy of the M–L π-interaction which ensures its additional stabilisation, is optimum when the cluster has the D_{4h} symmetry. Indeed, for bidentate ligands such as the O_2CR groups, the D_{4h} form does in fact ensure the most favourable conditions for the formation of a single system of delocalised π-bonds in the $M_2(O_2CR)_4$ cluster with participation of both M atoms in the ligands. Such a system of delocalised π-bonds is illustrated schematically in Fig.3 for each half fragment of the $M_2(O_2CR)_4$ cluster; this scheme can probably be extended also to the M–M and M–L π-bonds. The results of quantum-chemical calculations, on the basis of which the above conclusions have been reached, do not conflict with the X-ray electronic spectra of $M_2(O_2CR)_4$.[59–61]

Thus, for monodentate ligands (M_2Cl_8 dinuclear chloride clusters), the stabilisation of the D_{4h} form of the cluster is impossible without the formation of the M–M δ-bond. On the other hand, the stability of the D_{4h} form of the $M_2(O_2CR)_4$ carboxylate clusters must be accounted for by the bidentate character of the O_2CR ligands and the above characteristics of M–M and M–L π- and possibly σ-bonds in these dinculear clusters rather than by the presence of an M–M δ-bond.

The fact that the D_{4h} M_2Cl_8 chloride clusters exist only for M atoms with a d^4 electronic configuration, i.e. when eight valence electrons participate effectively in the M–M bond and when this two-centre bond is in fact quadruple (all the bonding σ, 2π, and δ molecular orbitals of the M–M bond are occupied by electrons, while the corresponding antibonding MO are unoccupied) with a strong δ-component constitutes convincing evidence for the above explanation. Even for a slight deviation of the electronic configuration of the M atom from the d^4 configuration to one side or another, i.e. for any change in the number of electrons involved in the M–M bond, the D_{4h} M_2Cl_8 chloride clusters are not as a rule formed. In this situation the formation of the δ-component of the M–M bond is impossible owing to the absence of valence electrons in the bonding δ molecular orbital of the M–M bond (when the total number of electrons in the two-centre M–M bond is less than eight) or owing to the appearance of electrons in the antibonding δ^* molecular orbital (when the total number of electrons is greater than eight).

On the other hand, the $M_2(O_2CR)_4$ carboxylate clusters exist in the D_{4h} form not only for the d^4 electronic configuration of the M atoms, when a quadruple M–M bond with a strong δ-component is formed, but also for large deviations from these configurations—for d^5, d^6, and even d^7 M atoms when the δ-component of the M–M bond is absent and the two-centre M–M interaction is as a whole significantly weakened. Indeed, the electronic structure of the two-centre M–M bond in the $M_2(O_2CR)_4$ clusters is quite varied: ranging from a quadruple M–M bond with a high energy in the molybdenum and rhenium clusters to the M–M bond with a reduced energy and multiplicity in the ruthenium and rhodium clusters, where the effective numbers of electrons in the M–M bonds are much greater than eight (Table 2).

The increase of the M–M distance and the paramagnetism of the complexes $Ru_2(O_2CC_3H_7)_4Cl$ and $Rh_2(O_2CCH_3)_4.2H_2O$ show that the M–M bonds in the complexes are significantly weakened; they are apparently triple ($\sigma + 2\pi$) and not quadruple ($\sigma + 2\pi + \delta$) and do not include a δ-component, because the excess (above eight) valence electrons in $Ru(O_2CC_3H_7)_4^+$ (eleven electrons) and $Rh_2(O_2CCH_3)_4$ (fourteen electrons) populate only the antibonding M–M δ^*-molecular orbital, i.e. they prevent the appearance of the δ-component in the M–M bonds; the remaining excess electrons populate the antibonding MO of the M–L bonds (Fig.2). The M–M antibonding $2\pi^*$ and σ^* MO still remain unoccupied under these conditions; this preserves the M–M triple ($\sigma + 2\pi$) bond in the cluster, which is apparently characteristic of $Ru_2(O_2CR)_4^+$ and $Rh_2(O_2CR)_4$.

Table 2. Electronic structure parameters of M–M bonds in the $M_2(O_2CR)_4$ clusters.

Parameter	Cluster			
	$Mo_2(O_2CR)_4$	$Re_2(O_2CR)_4^{2+}$	$Ru_2(O_2CR)_4^+$	$Rh_2(O_2CR)_4$
Electronic configuration of M atoms	d^4	d^4	d^5—d^6	d^7
M–M distance, Å	2.11	2.24	2.28	2.45
Multiplicity of M–M bond	$4(\sigma+2\pi+\delta)$	$4(\sigma+2\pi+\delta)$	$3(\sigma+2\pi)$	$3(\sigma+2\pi)$
No. of valence electrons in M–bond	8	8	11	14
References	[17, 59]	[17, 59]	[17, 59]	[17, 59]

A strong influence by the bidentate O_2CR ligands on the stereochemistry of the clusters is also manifested by the fact that the D_{4h} M_2Cl_8 chloride clusters are stable only for heavy (4*d*, 5*d*) elements, while the dinuclear D_{4h} $M_2(O_2CR)_4$ carboxylate groups are stable also in the case of light (3*d*) elements; an example of this is provided by the dimeric copper and chromium acetates.

3. The Conformational Transformations of Carbonyl Clusters

Transition metal chloride and carbonyl clusters have significantly different stereochemistries, particularly in the case of the heaviest (5*d*) transition elements: the differences consist in the fact that the ligands in the chloride clusters very often form bridge bonds with the M atoms, while in the carbonyl clusters all the ligands are always terminal.

One of the main stereochemical characteristics of the carbonyl clusters is their tendency towards the *trans*-disposition of the CO groups relative to the M–M bonds, i.e. approximately along the line of the two-centre M–M bonds. Owing to the absence of the π-component in the M–M bonds in the carbonyl clusters, such dispotion of the ligands is most favourable for the formation of strong dative M–CO π-bonds, i.e. for the maximum energy stabilisation of the carbonyl cluster as a whole.[21,22,62] In particular, such are the molecular and electronic structures of the $Ir_4(CO)_{12}$ tetrahedral carbonyl cluster with T_d symmetry[63,64] (Fig.4). However, steric factors prevent the ideal *trans*-disposition of the CO groups relative to the two-centre M–M bonds; these groups are "deflected" towards the centre of the Ir_4 tetrahedron and the C–Ir–Ir valence angle is 150°, i.e. much less than 180°. Such distortion of the molecular structure of the $Ir_4(CO)_{12}$ leads to some destabilisation of the dative Ir–CO π-bonds.

In the isoelectronic tetranuclear $Co_4(CO)_{12}$ carbonyl cluster the M–CO bonds are much shorter[40] and the steric limitations under discussion therefore increase so sharply that $Co_4(CO)_{12}$ with a tetrahedral structure becomes energetically unstable:

the CO groups in the tetrahedral $Co_4(CO)_{12}$ would have been too remote from the *trans*-disposition relative to the two-centre M–M bonds, for which the formation of strong dative M–CO π-bonds is possible. It is therefore likely that $Co_4(CO)_{12}$ has a conformation different from that of $Ir_4(CO)_{12}$ and in the energetically stable state assumes the C_{3v} molecular structure, where three out of the twelve ligands are of the bridging type (Fig.4).

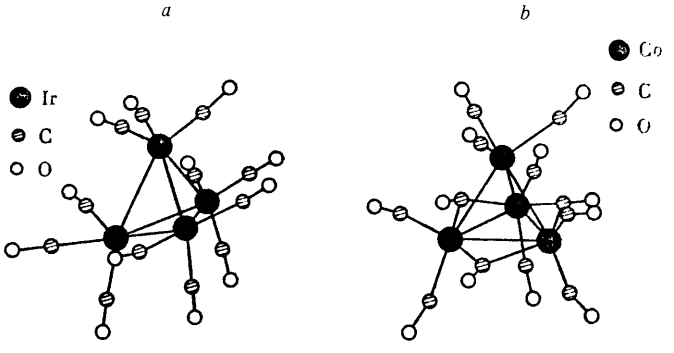

Figure 4. The molecular structure of tetranuclear carbonyl clusters: *a*) $Ir_4(CO)_{12}$ (T_d); *b*) $Co_4(CO)_{12}$ (C_{3v}).[62]

An analogous phenomenon for $Ir_4(CO)_{12}$ is hardly feasible. The appearance of bridging CO groups in the molecular structure of any carbonyl clusters requires that the M–M and M–CO bond lengths must meet severe requirements, rigorously specified by the extent and angular distribution of the virtual (unoccupied by electrons in free CO molecules) $2\pi^*$ MO of the CO groups, the only ones which can give rise to dative M–CO π-bonds necessary for the existence of the carbonyl cluster. Indeed in all the carbonyl compounds with bridging CO groups without exception, the M–C–M valence angle lies within very narrow limits (80–87°).[65] Clearly, on passing from atoms of 3*d* elements (Co) to those of 5*d* elements (Ir), which are characterised by a much greater extent of the valence orbitals, the necessity for the preservation of the angular distribution characteristic of the bridging M–C–M group would lead to such a marked deviation of the M–CO bond lengths from their normal values in the carbonyl cluster of a 5*d* element with bridging ligands that sufficiently strong M–CO bonds (primarily σ-bonds) could hardly exist at all.

However, on the whole, the bridging CO groups as a rule stabilise the carbonyl cluster and the only limitation is the "rigidity" of the valence electronic structure of the CO group. This is precisely the reason why carbonyl clusters with bridging ligands are formed mainly by 3*d* elements, while 5*d* elements produce carbonyl clusters solely with terminal ligands [$Os_3(CO)_{12}$, $Ir_2(CO)_8$, $Ir_4(CO)_{12}$, etc.[40]]. The clusters of 3*d* elements [$Fe_3(CO)_{12}$, $Co_2(CO)_8$, $Co_4(CO)_{12}$, etc.] can exist both in the form with bridging ligands (this is most characteristic of such clusters) and in the form incorporating only terminal ligands. In this sense the conformational transformations of carbonyl clusters constitute an entirely realistic physical process. The appearance of a carbonyl cluster of a 3*d* element in the form without a bridging ligand requires special conditions (high temperature, molecular solutions) ensuring the energy activation necessary for such a conformational transformation.[65]

The carbonyl clusters of 4*d* elements occupy a intermediate position in this respect: in some cases they incorporate bridging CO groups [$Rh_4(CO)_{12}$], while in others all the ligands are terminal [$Ru_3(CO)_{12}$, $Rh_2(CO)_8$].

The inability of the 5*d* elements to form carbonyl clusters with bridging CO groups has an important consequence: the 3*d* and 4*d* elements in a particular Group in the Periodic System form carbonyl clusters of a kind which are absent for the heaviest (5*d*) transition metals. As an example, we may point to the stability of $Fe_2(CO)_9$, $Co_6(CO)_{16}$, $Rh_6(CO)_{16}$ and the absence of analogous derivatives of osmium and iridium.[40,42]

The causes of the preferential existence of the chloride clusters of 5*d* elements in a form involving bridging ligands and the absence of bridging ligands from molecular structures of the carbonyl clusters of these *d* elements have been discussed in detail[66] on the basis of the results of calculations for one-electron molecular orbitals of the trinuclear $Re_3Cl_{12}^{3-}$ and $Os_3(CO)_{12}$ groups.

Thus the absence of M–M π-bonds and, what is most important, the angular distribution of the valence $2\pi^*$ MO of the CO groups forming the dative M–CO π-bonds explain the conformational transformations of the carbonyl clusters of 3*d* elements, their existence in the form of molecular structures with bridging ligands, and the absence of similar phenomena in the chemistry of the cluster carbonyls of 5*d* elements.[21,62]

4. Oxygen-containing Cluster Compounds of 4*d* and 5*d* Elements and Their Characteristic Features; Intercluster Interactions

The influence of the ligand environment on the structure of the clusters and on the electronic structure of their M–M bonds is manifested particularly strikingly in the case of the cluster oxides. Distinctive clusters with oxygen atoms as ligands have been discovered so far for a comparatively small number of transition metal oxides: $La_4Re_6O_{19}$ (Re_2 groups), $Au_2^{II}Mo_3O_8$, and $A_2^{II}W_3O_8$ (where A^{II} = Mg, Mn, Fe, Co, Ni, Zn, or Cd) (Mo_3 and W_3 groups), $Ba_3Ru_3O_9$ (Ru_3 group), and certain others.[25,40,67–81] The oxygen clusters are formed only by 4*d* and 5*d* elements (clearly identified oxygen clusters of 3*d* elements have not so far been discovered) and in addition by elements in the middle of the transition series only.

We may note that in the crystal structures of the dioxides strong M–M bonds exist only for the 4*d* and 5*d* elements precisely in Groups VI and VII of the Periodic System (MoO_2, WO_2, TcO_2, and ReO_2, where the M–M bonds are probably double). On the other hand, in the dioxides NbO_2 and TaO_2 these bonds are greatly weakened and in the platinum group metal dioxides (RuO_2, OsO_2, etc.) the M–M bonds are most probably absent; the M–M bonds are known *a priori* to be absent from ZrO_2 and HfO_2, because of the highest oxidation state of the metal. The transition to 3*d* elements is accompanied by a sharp decrease of the strength of the M–M bonds and their disappearance (VO_2, CrO_2, MnO_2, CoO_2, etc.).

In the oxygen clusters (as well as chloride clusters) the M–M bonds arise with the preferential involvement of the valence *d* electrons of the M atoms and can be both single and multiple (in particular, double). However, in contrast to the chloride clusters, in the chloride clusters the M–L bonds have a multiplicity greater than unity (with a considerable π-contribution) and the M–M and M–L interactions are not isolated; on the other hand, the inter-relation between the M–M and M–L interactions (the mixing of the molecular orbitals of these bonds with respect to energies and the

contribution of the M and L atomic orbitals) constitute a permanent element in the structure of any oxygen cluster. The M–M bonds in such clusters (particularly the π-components) are formed with participation of the bridging oxygen atom; the decisive role of the bridging oxygen atoms in the formation of a system of delocalised π-bonds between the metal atoms is apparently the cause of the absence of non-bridged oxygen clusters. In an oxygen cluster the bridging ligands promote the delocalisation of the valence electrons of the M atoms over the M–M bonds of the π-type; the mixing of the molecular orbitals of the M–M and M–O bonds takes place owing to the transfer of electron density from the bridging oxygen atoms, which behave as π-donors (this effect is characteristic of polynuclear oxygen complexes, without it, such complexes apparently could not exist).

All these distinctive features of the electronic structures of oxygen clusters can be traced quite reliably (both experimentally and theoretically), in particular in the trinuclear $Mo_3O_{13}^{14-}$ and $Ru_3O_{12}^{12-}$ groups.[67,79,80] A specific feature of the M–M and M–O π-interactions in the oxygen clusters, noted above, explains an unexpected characteristic of the electronic structure of the $Ru_3O_{12}^{12-}$ (Fig.5), namely that the M–M π-bonds in the linear Ru_3 group (with Ru–Ru double bonds) are formed not only between neighbouring metal atoms [Ru(1)–Ru(2), (Ru(2)–Ru(3)] but also directly between the terminal metal atoms [Ru(1)–Ru(3)], separated from one another by "bridging" M atoms [Ru(2)]. On the other hand, both M–M σ-bonds are to a marked extent localised in the two-centre Ru(1)–Ru(2) and Ru(2)–Ru(3) fragments.

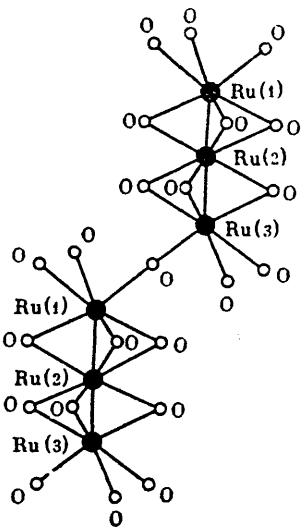

Figure 5. The $Ru_3O_{12}^{12-}$ (or $Ru_3O_6O_{6/2}^{6-}$) fragments of the crystal structure of barium ruthenite $Ba_3Ru_3O_9$.[78]

The results of the analysis of the magnetic properties of the $Ba_3Ru_3O_9$ crystal and of the characteristic features of the exchange interaction in the isolated $Ru_3O_{12}^{12-}$ cluster, carried out[79] within the framework of the Heisenberg–Dirac–Van Vleck model (which makes it possible to investigate the magnetism of cluster paramagnetic compounds), are fully consistent with the presence of two unpaired electrons in the MO of $Ru_3O_{12}^{2-}$ and with the strong electronic interaction of the terminal metal atoms in the linear Ru_3 cluster. The terminal atoms in the Ru_3 trimer are only formally geometrically isolated from one another. Apparently the M atoms in the cluster tend to equalise their states, not only by forming groups in which the M atoms are known to be equivalent (for example triangular Mo_3 clusters, as in $Mo_3O_{13}^{14-}$) but also by forming bonds between M atoms "not in contact" and which are in addition separated by the "third" M atom. In the linear Ru_3 cluster all three M atoms are probably in similar electronic states, which in no way follows *a priori* from its steterochemistry. [On the contrary, the non-equivalence of the electronic states of the middle Ru(2) atom, on the one hand, and the terminal Ru(1) and Ru(3) atoms, on the other, should seemingly follow from the geometry of the linear Ru_3 cluster.]

In cluster oxides the ligand environment not only determines in many respects the electronic structure of the M–M bonds but (and this is particularly important) is responsible for the strong intercluster interaction in the crystal structure. The bridging oxygen atoms, each linking two M atoms in different "neighbouring" clusters, ensure (also as a result of the formation of π-donor bonds with each M atom of this kind) the appearance of a single system of delocalised M–M and M–O π-bonds with the simultaneous participation of all the clusters (i.e. ensures the delocalisation of the valence π-electron density of the M atoms over all the clusters at once). Such strong intercluster interaction (Fig.5) is distinctly reflected in almost all the properties of the corresponding crystal and in the first place is manifested by a high conductivity ($Ba_3Ru_3O_9$, for example, exhibits metallic conductivity[78]). In contrast to this, in the cluster chlorides (which are dielectrics) such delocalisation of the valence electron density of the M atoms is negligible and in this sense one may speak of the absence of an appreciable intercluster interaction in their crystal structures.

V. THE EFFECTS OF CLUSTER FORMATION

The formation of cluster groups in crystalline structures of transition metal compounds naturally makes its own impression to a greater or lesser extent on all the physical characteristics of these compounds and this distinguishes them from the corresponding mononuclear complexes. Evidently the first in these series of properties should be the specific characteristics of the crystal structures of the cluster compounds which are revealed in X-ray diffraction studies, showing that groups of several (two or more) M atoms in direct contact, which are more or less isolated from one another, exist in the crystal;[31–40] the M–M internuclear distances within the limits of such groups are close to the values for the corresponding metallic crystal or even much smaller. The distances between the M atoms in different (neighbouring) clusters are as a rule much greater.

This factor by itself indicates the formation of M–M bonds in the cluster crystal together with the usual M–L bonds. The formation of M–M bonds has been confirmed by the magnetic properties of cluster compounds (or at least the latter do not conflict with their formation):[31–40] in the vast majority of cases the effective magnetic moments of cluster compounds are greatly reduced (down to the diamagnetic level) compared with the values expected on the basis of the formal valence of the M atom. Here we have in mind the following situation. In a cluster compound the M atoms always have a low formal valence (this is a permanent condition for cluster formation) and therefore several valence electrons (d^m), not involved in bonding to the ligands and responsible for the very high paramagnetism, should therefore remain in

each M atom. However, owing to the pairing of the spins of the valence electrons of the M atoms in the M–M bonds, the experimental effective magnetic moment of cluster compounds is always much less than the value expected for the d^m configuration and not only in terms of the approximation of the spin only values but also when account is taken of effects such as spin–orbital coupling, antiferromagnetism, etc.[27,34]

The formation of clusters with strong M–M bonds makes an important additional contribution, additional to that of the M–L bonds, to the total energy of the crystal structure. The energy effects of cluster formation (the M–M bond energies) in the chlorides and oxides of heavy *d* elements and in the carbonyls and certain other compounds of transition metals have been estimated from the enthalpies of formation of these compounds,[4,23,24,34,79,82–84] by semi-empirical calculation of the molecular orbitals of the corresponding isolated clusters,[2–4,12,21,23,51,79,84] and even by direct mass-spectrometric measurement of the energies of dissociation of clusters into mononuclear fragments.[85]

Both experimental and theoretical results have shown that the M–M interaction energies in the cluster chlorides and oxides with heavy *d* elements (calculated per electron involved in such interactions) are usually in the range 25–35 kcal, i.e. the structure is fairly stable despite the fact that these compounds include clusters of different *d* elements, with different formal valences of the M atoms, and with extremely different stereochemistries. This range is in fact most characteristic of the M–M interaction energies in the metallic crystals of 4*d* and 5*d* elements; the latter factor indicates that the formation of an M–M bond in clusters is one of the principal energy factors ensuring the compensation of the endothermic effect of the breakdown of the structure (i.e. the compensation of the enthalpy of atomisation) of the crystal of the transition metal on formation of its formally low-valence chlorides and oxides. At the same time, the stability indicated by the E_{M-M} values does not rule out the formation (particularly in chloride clusters—Table 3) of two-centre M–M bonds with different energies up to very high values, depending on the number of electrons in these bonds and hence on the M–M distances.

Table 3. Parameters of the two-centre M–M bonds in the chloride and carbonyl clusters.

Cluster	R_{M-M}, Å	n_{M-M}	E_{M-M}, kcal	k_{M-M}, mdyn Å^{-1}	Refs.
$Re_2Cl_8^{2-}$	2.24	8	270	4.2	[6]
$Mo_2Cl_8^{4-}$	2.14	8	297	3.4	[6, 53]
$W_2Cl_9^{3-}$	2.41	6	155	1.2	[26]
$W_6Cl_8^{4+}$	2.61	2	59	0.3	[26]
$Mo_6Cl_8^{4+}$	2.61	2	44	0.3	[26]
$Nb_6Cl_{12}^{2+}$	2.92	1.3	34	0.3	[2]
$Ta_6Cl_{12}^{3+}$	2.93	1.2	33	0.3	[2]
$Mn_2(CO)_{10}$	2.92	2	17	0.6	[22]
$Tc_2(CO)_{10}$	3.04	2	31	0.7	[22]
$Re_2(CO)_{10}$	3.02	2	38	0.8	[22]
$Os_3(CO)_{12}$	2.88	2	28	0.9	[66]
$Ir_4(CO)_{12}$	2.68	2	31	1.2	[64]

Notation: R_{M-M} is the M–M distance, n_{M-M} the number of valence electrons per two-centre M–M bond, E_{M-M} the energy of this bond, and k_{M-M} the force constant of the M–M stretching vibrations.

In the carbonyl clusters of 4*d* and 5*d* elements the M–M interaction energies (also calculated per electron) are lower by a factor of approximately 1.5–2.[4,20,85] The cause of this is that in the electronic structure of a carbonyl cluster the bonding σ MO responsible for the M–M bonds have an enhanced energy, because these MO are at the same time antibonding in relation to the M–*trans*-CO σ-interactions and in addition a large contribution to such orbitals comes not only from the $(n-1)d$ MO but also from the valence *np* orbitals, having an increased electron energy, of the M atoms. Furthermore, one should bear in mind that single (two-electron) two-centre M–M bonds of the σ-type are usually formed in carbonyl clusters (without an appreciable π-contribution), the bonds having comparatively large internuclear distances.

Thus the large contribution of the M–M bonds to the total energy of the cluster confirms the dominant role of the M–M interactions in the phenomenon of cluster formation (particularly in compounds of the formally low-valence chlorides and oxides of 4*d* and 5*d* elements) and the principal cause of the existence of clusters may be seen in the high M–M bond strength.

VI. SPECTROSCOPY OF CLUSTER COMPLEXES

The formationof clusters is manifested in EPR, NQR, Mössbauer, and magnetic circular dichroism spectra.[11,86–90] However, cluster formation is revealed most directly in optical, vibrational, X-ray emission, and X-ray electronic spectra; the last spectra yield the most direct information about the states of the valence electrons of the M atoms and ligands, about the valence of the M atoms, about the nature of the M–M bonds in the clusters, and about the electronic structure as a whole and also reveal the qualitative and quantitative characteristics of cluster compounds which are absent from mononuclear complexes; these appreciable differences between the properties of cluster and mononuclear compounds reflect the phenomenon of cluster formation.

1. Optical Electronic Spectra

The experimentally observed absorption maxima in the optical electronic spectra of cluster compounds mainly reflect the electronic transition from the occupied bonding MO of the M–M bonds to the corresponding unoccupied non-bonding or antibonding MO. These are "metal–metal" transitions, which are apparently characteristic of clusters in general, but have been most thoroughly investigated in the cluster chlorides of 4*d* and 5*d* elements.[11,26,27,51,92–103]

The generally accepted interpretation of the optical electronic spectra is based in this instance on the hypothesis that one-electron transitions involving the M–M MO, delocalised in the clusters between the M atoms and having a predominantly *d*-electron character, are mainly responsible for the absorption in the visible region of the spectra. Despite this assumption, the long-wavelength electronic transitions in the spectra of the compounds investigated reflect fairly accurately the electronic structure of the M–M bonds in the clusters: the number of bands, their positions in the spectrum, and their relative intensities agree with the number of MO of the M–M bonds, their energy sequence, their electron populations, and finally their symmetry, which makes it possible to distinguish (within the framework of the selection rules for the optical spectrum) the allowed and forbidden transitions.[26,51]

In contrast to the cluster compounds, the optical electronic absorption spectra of complexes without an M–M bond can be simply described in terms of *d*–*d* transitions significantly localised at each M atom; for this reason, the form of the spectrum constitutes an indication of the cluster or mononuclear nature of the complex.

2. Vibrational Spectra

In the study of cluster compounds by vibrational spectroscopic methods attention is naturally concentrated on the vibrations of the M–M bond, which can be regarded as characteristic for such bonds (apart from a small contribution by M–L bonds only). This characteristic nature of the vibrations consists in the fact that the optical absorption spectra of cluster compounds in the infrared range contain bands at frequencies in the range 100–400 cm^{-1}, frequencies closer to the lower limit being characteristic of clusters with comparatively weak (single) M–M bonds, while frequencies characteristic of clusters with very strong (quadruple) M–M bonds lie near the upper limit of the above range.

The results of studies on cluster transition metal chlorides, oxides, and carbonyls by infrared and Raman spectroscopic methods,[11,79,103–121] namely the ν(M–M) frequencies and k_{M-M} force constants for the two-centre M–M bonds, yield information about the strength of these bonds. The available data (presented in part in Table 3) make it possible to compare the force constants (or frequencies) of the stretching vibrations, the effective numbers of electrons, the energies, and the internuclear distances for the two-centre M–M bonds in clusters. The correlations between these characteristics are unambiguous and usually reveal a parallel variation of $k_{M-M}[\nu(M-M)]$, n_{M-M}, and E_{M-M}, in particular their increase as the M–M distances are shortened.

The situation is more complex in cluster oxides in the presence of strong intercluster interactions. Whereas in the infrared spectra of $Mg_2Mo_3O_8$ and $Zn_2Mo_3O_8$, where the internuclear interaction is comparatively weak, the stretching vibration frequencies of the Mo–Mo bonds in the trinuclear Mo_3 clusters are manifested (at approximately 200 cm^{-1}),[79] in the infrared spectra of $Ba_3Ru_3O_9$, MoO_2, WO_2 and RuO_2 with strong (double) M–M bonds, there is virtually no absorption in the frequency range 100–1700 cm^{-1}, i.e. the M–M stretching vibrations are not shown.[79] This can be accounted for by the specific features of the $Ba_3Ru_3O_9$, MoO_3, WO_2, and RuO_2 structures expressed by the fact that these compounds have, instead of an island structure, a coordination structure, which ensures their metallic conductivity[121] and precludes the manifestation in the spectrum of vibrations localised in the quasi-molecular fragments.

3. X-Ray Emission Spectra

The cluster chlorides and oxides with certain 4*d* elements, mainly Nb, Mo, and Ru,[4,79] have been most fully investigated by this method. The L_{β_2} and L_{γ_1} lines of the M atoms, which reflect the distribution of the valence 4*d* electrons of the M atoms, responsible for the formation of the M–M bonds, among the occupied MO of the clusters, have been used for the X-ray spectroscopic study of the valence electron structures of these M atoms. Fig.6 presents as an example the L_{β_2} spectrum of molybdenum in $Cs_3Mo_2Cl_8$. The X-ray spectra of cluster chlorides, which yield information about the energy sequence of the occupied MO of the cluster, the electron populations, the contributions to the MO by the valence 4*d* orbitals of the M atoms, etc., permit the following conclusions:

(1) The 4*d* orbitals of the M atoms make the main contribution to the M–M MO, which have the highest energies and lie above the MO of the M–Cl bonds, formed predominantly with the participation of the 5*p* orbitals of the M atoms, this implies that the M–M and M–L electronic interactions are in this instance truly isolated from one another to a large extent with respect to both the energies of the MO responsible for such interactions and the contributions of the valence atomic orbitals (AO).

(2) The 4*d* electrons of the M atoms participate mainly in the M–M bonds and to a much lesser extent in the M–Cl bonds; the M–M interactions, which are predominantly of the *d*-electron type, are largely localised within the limits of the M_n group of the "metallic nucleus" of the cluster.

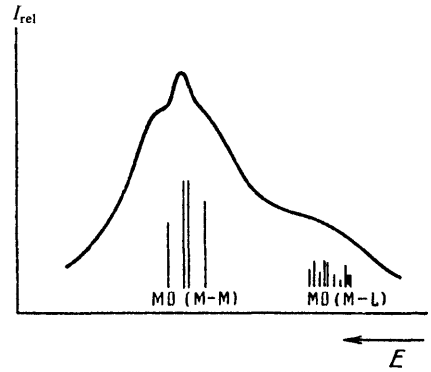

Figure 6. The X-ray emission L_{β_2} spectrum of molybdenum for $Cs_3Mo_2Cl_8$.[4]

At the same time the parameters $K_{\beta_{1,3}}$ of the line due to chlorine in the X-ray spectra of the same cluster chlorides show[4] that not all the valence 3*p* electrons of the Cl atoms are involved in the M–Cl bonds without conflicting with the idea that mainly M–Cl σ-bonds are formed with a low π-contribution to the metal–ligand interaction and that a large proportion of the $3p\pi$ electrons of the Cl atoms remain in a pseudoatomic state.

The X-ray spectra of cluster oxides have a somewhat different appearance. In the oxygen cluster the occupied MO are of a "mixed" character (they are simultaneously responsible for the M–M and M–O bonds) and the valence 4*d* orbitals of the M atoms make a considerable contribution to all these MO, including the MO of the M–L bonds. In the oxygen cluster the MO with a large contribution by the *d* AO of the metal therefore have a much greater energy range than in the chloride cluster, where the large (sometimes predominant) contribution of the *d* AO of the metal is present only in the highest-energy occupied MO, responsible almost exclusively for the M–M interactions, and not in the MO of the M–Cl bonds. The energy range including the MO of the chloride cluster with a large contribution by the valence *d* orbitals of the M atoms is much narrower.

All this ultimately explains why the X-ray spectra of the metal, reflecting the distribution of the valence *d* electrons of the M atoms among the molecular orbitals of the clusters (this applies particularly to the L_{β_2} spectrum of molybdenum), contain a wider band in the case of the cluster oxide (with a large involvement of the *d* electrons of the M atoms in the M–L bonds) than in the cluster chloride (with a small involvement of the *d* electrons of the M atoms in the M–L bonds) of the same transition metal.[79]

The study of the chemical shifts of the emission lines (*K*, *L*, etc.) of heavy *d* elements in the X-ray spectra of their various compounds yields important information. The results of

measurements of the chemical shifts of the K and L lines of Nb, Mo, and W in the X-ray emission spectra of numerous cluster and mononuclear compounds are available.[4,122-124] The chemical shifts ΔE have been measured for cluster compound–corresponding metal pair combinations. It has been found that the ΔE peaks for the metal increase linearly with increase of the formal valence of the M atoms for the chlorides in the structures of which there are no clusters and M–M bonds are known to be absent; Fig.7 presents as an example the values of ΔE(Nb) in the system of niobium chlorides. The linearity in the variation of the ΔE can be explained by the successive changes in the effective number of valence electrons of the M atoms not involved in bonding to ligands and localised in the pseudoatomic 4*d* or 5*d* states based on the M atom. The number of such electrons n is equal to the difference between the total number of valence electrons of the M atoms and their formal valence V_M, i.e. the number of their valence electrons in the M–Cl bonds. The observed linearity of the variation, implying proportionality of the changes in ΔE when the number of the unbound 4*d* or 5*d* electrons of the M atom is altered, corresponds to the overall physical nature of the effect of the chemical shifts of the X-ray lines.[125]

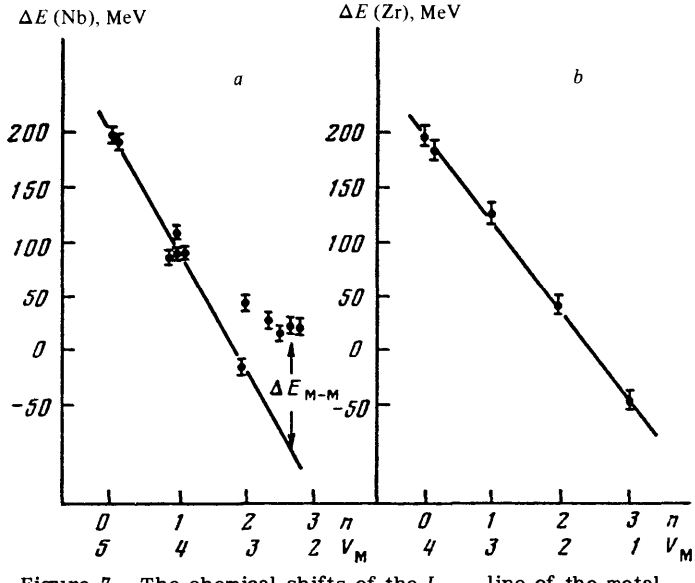

Figure 7. The chemical shifts of the $L_{\alpha_{1,2}}$ line of the metal (ΔE) in the X-ray spectra of niobium (*a*) and zirconium (*b*) chlorides as a function of the formal valence of the metal V_M and the number n of the valence electrons of the M atom not involved in the M–Cl bonds:[4,124] *a*: 1) $NbCl_5$; 2) $KNbCl_6$; 3) $NbCl_4$; 4) K_2NbCl_6; 5) Rb_2NbCl_6; 6) Cs_2NbCl_6; 7) $Cs_3Nb_2Cl_9$; 8) K_3NbCl_6; 9) Nb_3Cl_8; 10) $CsNb_4Cl_{11}$; 11) Nb_6Cl_{14}; 12) $K_4Nb_6Cl_{18}$; *b*: 1) $ZrCl_4$; 2) Na_2ZrCl_6; 3) $ZrCl_3$; 4) $ZrCl_2$; 5) ZrCl.

The chemical shifts of the lines in the X-ray spectrum of the metal for cluster compounds always deviate sharply from the linear relation characteristic of mononuclear compounds (Fig.7). These deviations reflect appreciable delocalisation of the valence 4*d* or 5*d* electrons of the M atoms not involved in bonds with the ligands, i.e. they reflect the effective electronic interactions between the metal atoms in the cluster chlorides. The "anomalous" values of ΔE thereby indicate directly the formation of M–M bonds in the chloride clusters. These deviations (ΔE_{M-M}) from the linear relations increase in proportion to the increase of the number of the valence electrons of the M atom which are not involved in the M–Cl bonds and are therefore fully available for involvement in the M–M interactions.

In the series of chlorides of the same heavy *d* element incorporating M atoms with the same formal valence, the deviations of ΔE from linearity, due to the M–M interactions in the clusters, increase in succession with increase in the number of electrons in the M–M bonds and also with decrease of the M–M distances and the accompanying decrease of the effective magnetic moments, i.e. as the M–M bonds become stronger. This can be traced particularly clearly in relation to the chlorides of the formally tervalent molybdenum (Fig.8), where the limiting M–M distance (approximately 3 Å), which is the beginning of the range of distances in the chlorides of 4*d* and 5*d* elements for which clusters with M–M bonds are virtually not formed, is very clearly shown.

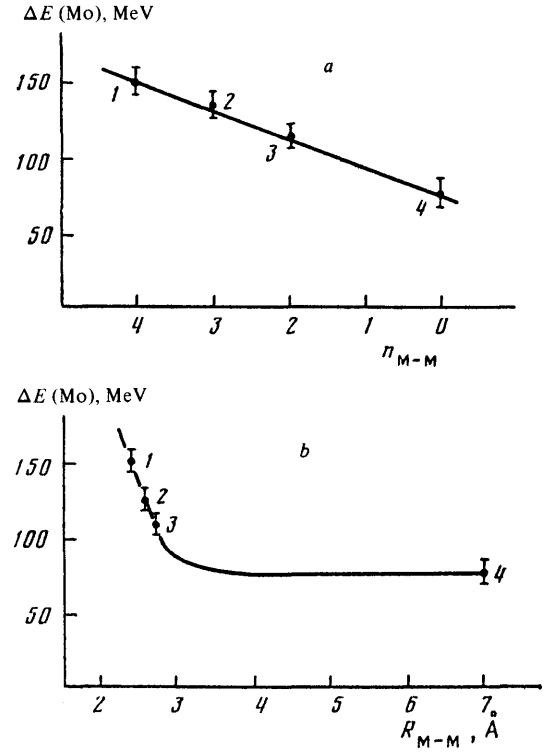

Figure 8. The chemical shifts of the $L_{\alpha_{1,2}}$ line of molybdenum ΔE in the X-ray spectra of the chlorides of the formally tervalent molybdenum as a function of the number n_{M-M} of the valence electrons of the M–M bonds (*a*) and the M–M distance R_{M-M} (*b*):[4,123] 1) $K_3Mo_2Cl_9$; 2) $Cs_3Mo_2Cl_9$; 3) $MoCl_3$; 4) K_3MoCl_6.

Study of the chemical shifts of the X-ray $L_{\alpha_{1,2}}$ line of molybdenum in the series of its formally low-valence chlorides with two-centre M–M interactions, i.e.

$$Mo_2Cl_{10}\,(MoCl_5) \underset{d^1}{} — \underset{d^2}{MoCl_4} — \underset{d^3}{MoCl_3} — \underset{d^3}{Cs_3Mo_2Cl_9} — \underset{d^3}{K_3Mo_2Cl_9} —$$
$$— \underset{d^3-d^4}{Cs_3Mo_2Cl_8} — \underset{d^4}{K_4Mo_2Cl_8}\ ,$$

has shown that, with increase of the number of 4*d* valence electrons of the Mo atom (d^m), not involved in bonds with the ligands, i.e. with decrease of the formal valence of the metal, the tendency towards M–M bond formation increases sharply: whereas in the Mo_2Cl_{10} (d^1) dimer direct M–M electronic interactions are completely absent, the Mo–Mo distances are 3.85 Å, and the chemical shift due to the involvement of the valence 4*d* electrons of the Mo atoms in the Mo–Mo bonds is zero, in the dinuclear $Mo_2Cl_8^{4-}$ (d^4) cluster there exists a quadrupole ($\sigma + 2\pi + \delta$) Mo–Mo bond, the Mo–Mo distances are 2.14 Å, and the chemical shift due to the involvement of the eight 4*d* electrons of both Mo atoms in the Mo–Mo interactions has proved to be the highest among those known.[123]

In addition, yet another important example clearly indicates the major role of the valence d^m electronic configuration of the metal atom in the formation of M–M bonds. In the series of compounds of the formally tervalent (d^3) molybdenum ($MoCl_3$, $Cs_3Mo_2Cl_9$, $K_3Mo_2Cl_9$), the ΔE differ markedly, which implies that the Mo atoms with the d^3 configuration form strong M–M bonds with increased multiplicity only under sterically favourable conditions and that the M–M distance is most likely to be the decisive factor in this instance. On the other hand, in the series of chlorides of formally bivalent (d^4) molybdenum the ΔE are almost identical despite the markedly different M–M distances and there is a sharp variation in sterochemistry from the dinuclear $Mo_2Cl_8^{4-}$ (D_{4h}) cluster to the hexanuclear $Mo_6Cl_8^{4-}$ (O_h) cluster; in this case the decisive factor is the effective number of electrons capable of forming direct M–M bonds.[4,123]

Thus the chemical shifts in the X-ray emission spectra of the cluster chlorides of heavy *d* elements reveal a delocalisation of the valence electrons of the M atoms in excess of that determined by the metal–ligand bonds, i.e. they do not correspond to the distance of M–Cl bonds alone in such compounds but can be accounted for by simultaneous M–M bond formation in the clusters. The ΔE constitute a direct conformation of the existence of effective M–M electronic interactions in the chlorides of heavy *d* elements.

4. X-Ray Electronic Spectra

The cluster chlorides, oxides, carbonyl, and carboxylates of certain heavy *d* elements have been investigated by X-ray electronic spectroscopy (ESCA),[126] which makes it possible to measure the energy distribution (orbital energies) of the valence electrons and also of the internal levels of the atoms in molecular complexes in crystals.

The X-ray electronic spectra of the valence region of the cluster compounds mentioned above[4,11,59–61,79,80,127–129] make it possible to determine the ionisation potentials (absolute energies) of the occupied MO, their electon populations, the contribution of the basis AO to the valence MO, and certain other characteristics of the electronic structure of the clusters. The parameters of these spectra refine and supplement the results of quantum-chemical calculations of the electronic structure of clusters. In particular, the photoelectron spectra (He-I–He-II) of trinuclear, tetranuclear, and hexanuclear carbonyl clusters confirm the calculated characteristics of the molecular orbitals of the M–M and M–CO bonds.[11,128] The photoelectron and X-ray electronic spectra of the dinuclear chloride and carboxylate d^4 complexes, M_2L_8, indicate directly the formation of the quadruple M–M bond.[59–61,127]

The parameters of the X-ray electronic spectra of the valence region of the chloride complexes indicate clearly the separation of the M–M MO from all the remaining MO and their position in the highest energy region: this is manifested particularly strikingly when the electronic structure of the same chloride cluster is described in terms of X-ray electronic and X-ray emission spectroscopic data.[129] In a concerted study of the electronic structure of the $Mo_2Cl_8^{4-}$ cluster[129] the energies of the internal Mo ($3d_{5/2}$) and Cl ($2p_{3/2}$) levels were measured in the X-ray electronic spectrum, while the energies of the L_{α_1}-Mo, L_{β_2}-Mo, K_{α_1}-Cl, and $K_{\beta_{1,3}}$-Cl X-ray lines were measured in the X-ray emission spectrum. Next the K_{α_1}-Cl and $K_{\beta_{1,3}}$-Cl spectra were superimposed on the valence ESCA spectrum on the same energy scale (Fig.9). It was then shown that the highest occupied MOs of the $Mo_2Cl_8^{4-}$ cluster do indeed represent the virtually pure 4*d* electronic states of the Mo atoms (multiple Mo–Mo bonds), while the energies of the MO involving the valence electrons of the ligands (Cl atoms) are much lower and reflect the existence of the M–L bonds and the $3p_\pi$ AO of the ligands.

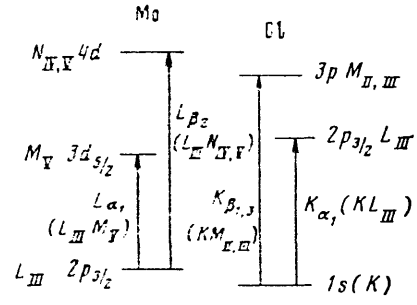

Figure 9. Schematic illustration of the method used in the superposition and the superimposed (with respect to energy) X-ray emission $K_{\beta_{1,3}}$.Cl (curve *1*), L_{β_2}.Mo (curve *3*) spectra and the X-ray electronic spectrum of the valence region of the $Mo_2Cl_8^{4-}$ cluster (curve 2).[129]

The X-ray electronic spectra of the valence region for cluster chlorides, oxides, and dimeric carboxylates with strong metal–metal bonds ($K_4Mo_2Cl_8$, $K_3Re_3Cl_{12}$, $K_3W_2Cl_9$, $Zn_2Mo_3O_8$, $Ba_3Ru_3O_9$, $Mo_2(O_2CCH_3)_4$, etc. differ appreciably from those for the corresponding mononuclear compounds of the same heavy *d* elements (K_3MoCl_6, K_2ReCl_6, K_2WCl_6, etc.). The formation of the cluster group (via the M–M bonds) in the structure of the chloride of a 4*d* or 5*d* element induces specific changes in the ESCA spectrum of such a cluster chloride (Fig.10). The formation of a cluster chloride with M–M bonds, whose electron density is concentrated in the "metallic nucleus" of the cluster, gives rise to significant changes in the interelectronic interaction in the polynuclear complex as a whole and "groups" the MO of this complex in terms of their energies in a specific manner.[4,59,60,79] It may be that the influence of the M–M bonds in the chloride cluster shortens the energy range within the limits of which the molecular orbitals of the M–L bonds, the pseudoatomic orbitals of the ligands, etc. are located compared with the greater possibilities for the energy distribution of the MO in a mononuclear complex. In this case it is understandable why the valence X-ray electronic spectra of the cluster chlorides consist of comparatively narrow bands grouped in terms of types of electronic interactions (M–M, M–L, AO–L, etc.).

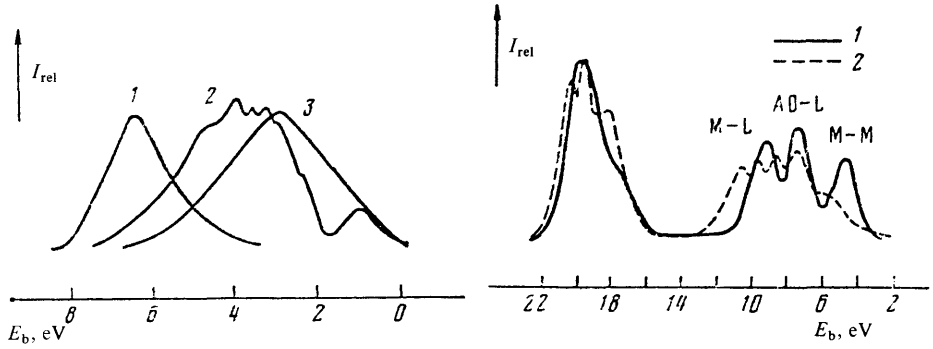

Figure 10. The X-ray electronic spectra of the valence regions in $K_3Re_3Cl_{12}$ (curve *1*) and K_2ReCl_6 (curve *2*).[6]

The experimental energies of the internal levels of the M atoms in the chlorides, dimeric carboxylates, and oxides of 4*d* elements (Mo, Ru) have led to the following finding (Fig. 11). In the series of mononuclear molybdenum chlorides these energies increase successively with increase of the formal valence of molybdenum on passing from the metal to the higher chlorides, which can be explained by the increase of the number of valence electrons of the Mo atom in the Mo–Cl bonds and the corresponding increase of the effective positive charge on the Mo atom. For the cluster molybdenum chlorides (particularly those with strong M–M bonds), the chemical shifts greatly exceed the corresponding values of ΔE(Mo) for mononuclear chlorides with the same formal valence of the metal; this effect is caused by the additional delocalisation (additional to that due to the M–Cl bonds) of the valence 4*d* electrons of the M atoms in the M–M bonds in the chloride clusters.[24] The effects of the chemical shift of the internal levels of the transition metal atoms in the X-ray electronic spectra as well as the chemical shifts in the X-ray emission spectra[122,123] indicate an increase of ΔE for the cluster chlorides compared with the mononuclear chlorides having the same formal valence of the M atoms.

The pattern of the chemical shifts of the $3d_{5/2}$ level for the M atoms is somehow more complex for mononuclear and cluster molybdenum and ruthenium oxides.[79,80] The cause lies in the special character of the metal–oxygen bonds, which apparently possess a donor–acceptor π-component (M⇇O or M⇇C⇉M), which promotes the "leakage" of the valence electronic charge to the M atoms, particularly on formation of clusters with M–M bonds, and also in the cooperative interactions in these crystals manifested by their electrical conductivity. However, here too the effects of cluster formation are fairly distinctive, although in a somewhat different form. Thus X-ray electronic studies of a series of formally heterovalent compounds of a heavy *d* element make it possible to observe the formation of clusters (particularly those with strong M–M bonds) and yield varied information about their electronic structure.

VII. THE NATURE OF THE M–M BONDS IN THE CHLORIDE CLUSTERS OF 4*d* AND 5*d* ELEMENTS

The X-ray spectroscopic chacteristics of the cluster chlorides of 4*d* and 5*d* elements provide a preliminary answer to the following question: what is the physical nature of the M–M bonds present in the chloride cluster? Do they resemble the bonds between the M atoms in the corresponding metals or do they represent a different type of interaction?

In any system of chlorides of the heavy *d* elements the appearance of valence *d* electrons of the M atoms in the M–M bonds (the formation of the cluster) and the further increase of their number immediately entail a deviation of the chemical shift of the X-ray *K* or *L* line of the metal (relative to the ΔE for the corresponding mononuclear chlorides without M–M bonds but with the same formal valence of the M atoms) in the direction of the highest chloride, where all the valence electrons of the M atoms are involved in the M–Cl bonds and where the maximum valence of the metal obtains. In other words, the formation of M–M bonds in a cluster chloride always shifts ΔE in the same direction as that which occurs with increase of the number of valence electrons of the M atom in covalent bonding to the ligands (M–Cl). The contributions to the overall chemical shifts of the *K* or *L* line of the metal in the X-ray spectrum of a cluster chloride due to the formation of M–Cl and M–M bonds always have the same sign.

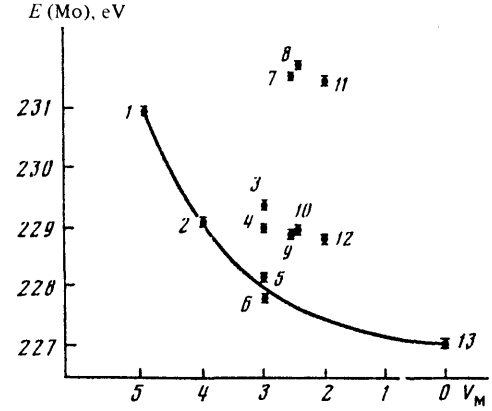

Figure 11. The energy of the $3d_{5/2}$ level in molybdenum atoms (E_b) in the X-ray electronic spectra of molybdenum chlorides as a function of the formal valence of molybdenum V_M.[4,124]

All this implies that the M–M bonds in the cluster chloride of a 4*d* or 5*d* element are formed in a manner similar to that of the M–Cl bonds. Precisely in this sense does the valence of the atoms of 4*d* or 5*d* elements in their cluster chlorides

greatly exceed (sometimes by a factor of 2–3) the formal value[3,30] determined by the involvement of a specific number of valence electrons of each M atom in the formation of M–Cl bonds alone.

Thus the M–M bonds in the cluster chlorides of heavy transition metals are close in their nature to the homoatomic covalent bonds. According to the results of molecular-orbital calculations,[4,11] the M–M bonds are localised (despite the fact that, with the exception of dinuclear clusters, they are many-centre bonds within the limits of the "island" cluster group) and different from the usual metallic bonds with their cooperative character.

If the M–M bonds in the chloride clusters resembled the usual metallic bonds in terms of the distribution of charge density of the valence electrons of the M atoms involved in them then measurement of the chemical shift relative to the lines due to the metal would have shown that the contribution to the overall chemical shift due to the formation of M–M bonds is zero. Consequently there would have been no deviations of ΔE (for cluster chlorides) from the linear relations observed for the mononuclear derivatives.

The latter is fully confirmed by the X-ray spectroscopic characteristics of zirconium chlorides.[124] The crystals of formally low-valence zirconium chlorides contain no clusters and have a chain or layer structure,[131] but the bonds between their M atoms are close to the usual metallic bonds in crystalline zirconium. Accordingly, the dependence of the chemical shift of the $L_{\alpha_{1/2}}$ line of zirconium on its formal valence and on the number of valence electrons of each zirconium atom not involved in bonds with the ligands is distinctly linear, which confirms the usual metallic nature of the M–M bonds with their cooperative character and the delocalisation of the valence electrons of the M atoms throughout the lattice of the non-cluster zirconium chlorides (ZrCl, $ZrCl_2$, or $ZrCl_3$; Fig. 7).

Thus the study of the chemical shifts of the emission *K* and *L* lines of heavy transition metals in the X-ray spectra of the mononuclear and cluster chlorides makes it possible to demonstrate the formation of M–M bonds in the clusters, to investigate the electronic structure of these bonds, and, what is most important, makes it possible to elucidate the nature of the M–M interaction in the cluster chlorides of 4*d* and 5*d* elements.

The cluster carbonyls, which frequently exist in the form of molecular crystals incorporating weakly interacting $M_n(CO)_m$ fragments, are apparently very closely related to the cluster chlorides, the main structural characteristic of which consists of the presence of a quasi-isolated "island" M_nX_n group. Cluster oxides constitute an example of crystal structures of a different nature—with a strong intercluster interaction and a high level of delocalisation of the valence electrons of the M atoms in the M–M bonds not only within the limits of the cluster but also between clusters in contact.

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Quantum-chemical and spectroscopic studies of chloride, oxide, carboxylate, and carbonyl clusters of 4*d* and 5*d* elements have revealed the fundamental principles of their electronic structure and showed, in particular, that direct (without a decisive influence of the bridging ligands) and effective (with a high energy) M–M bonds exist in the clusters. The corresponding MO indicate a high degree of delocalisation of the valence electrons of the M atoms in the M–M bonds, in excess of that which can be account for by M–L bonds, and the valence of the M atoms in the clusters is therefore always much higher than its formal value.

One of the main distinctive features of the electronic structure of the clusters is the spatial distribution of the electron density of the M–M bonds. Experimental and theoretical results[3,132] have shown that the electron density of the M–M bonds is localised mainly at the "metallic nucleus" of the cluster (at its M_n group), although in the oxygen (especially), carboxylate, and partly carbonyl clusters the nature of the M–M bond is much more complex owing to the inter-relation of the M–M and M–L interactions and also the intercluster interaction and the "spreading" of the valence electrons of the M–M bonds throughout the crystal. The characteristics of the distribution of the valence electrons of the M–M bonds in clusters (particularly in the chloride clusters but also apparently in many respects also in clusters with other ligands) impart to them properties significantly different from those of mononuclear complexes and probably playing a primary role in the catalytic activity of many cluster compounds.[133–137] The high catalytic activity of cluster complexes (particularly of their stereochemically open forms) in the catalysis of the redox reactions of small molecules, including photochemical reactions with participation of clusters in electronically excited states,[136,137] has been recently explained using the LCAO–MO and vibronic theories.[137]

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Estimation of the Stability of Clusters with the Aid of the Theory of the Electron Density Functional

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The likely usefulness of the application of simple versions of the theory of the electron density functional to the study of the energy characteristics of cluster compounds is discussed. Three types of cluster compounds are considered: clusters of elements as an intermediate form between a molecule and a solid, organometallic clusters, and organoelemental compounds of the *nido*-cluster type. The question of the variation of the bond energy in homoatomic clusters as a function of their size and steric structure is analysed.
The bibliography includes 104 references.

CONTENTS

I. Introduction 361
II. The electronic structure and energy characteristics of atomic clusters 365
III. Stability of organoelemental clusters 368

I. INTRODUCTION

The concept of the "cluster" has been widely used in recent years in various branches of chemistry. The constituent elements (atoms) of a chemical cluster are separated from one another by distances of the order of the chemical bond length and as a rule they form between one another the maximum possible number of bonds. The structural unit of the cluster is a regular or distorted polyhedron in which there are no classical two-centre chemical bonds characteristic of the usual molecules: the bonds in clusters have a many-centre character.

Since the beginning of 1970 metal clusters have been vigorously investigated by theoretical chemical methods (see the relevant reviews[1,2]). Qunatum-chemical study of these compounds within the framework of different versions of the non-empirical SCF LCAO-MO method presents significant difficulties, because the clusters contain a large number of electrons and non-empirical calculations for such systems are far beyond the scope of modern computer techniques. Semi-empirical methods (of the type of CNDO, INDO, MINDO, etc.), which have proved quite useful in organic chemistry, have proved fairly frequently to be inapplicable to transition metal clusters, because they lead to contradictory results.[3]

Quantum-statistical methods for calculations relating to complex compounds have been developing vigorously in recent years. The statistical method was initiated in the studies of Thomas, Fermi, and Dirac.[4] The Thoms-Fermi-Dirac (TFD) model has been widely used in a wide variety of fields such as nuclear, atomic, and solid state theories, astrophysics, etc.[5] The significant progress in the many-particle statistical theory has been associated with studies on the self-consistent theory of a non-uniform electron gas [the method of the electron density functional (MDF)]. The theorem that the determination of the energy of the ground state in the many-particle Schrödinger equation is equivalent to the determination of the minimum in the energy functional for a varying electron density has been proved.[6] By virtue of the theorems of the *V*- and *N*-representability of the electron density,[6-8] the method of the electron density functional has been theoretically justified.

The quantum-statistical many-particle theory has laid the foundations for a series of methods for the calculation of the electronic structure of molecules. These are in the first place different versions of the Slater-Johnson X_α method, in which a statistical exchange potential is introduced.[9] Furthermore, one should include here the discrete variation method,[10-12] which is a variety of the X_α method in terms of a basis set of atomic functions, and the local spin density (LSP) method.[13,14] The latter is a generalisation of the Hohenberg-Kohn-Sham theory[15] and differs from the Hartree-Fock scheme by taking into account all the many-particle effects at the level of the density functional. Apparently the above methods can be expected to be most successful in the solution of various problems of the theoretical chemistry of organometallic compounds, including cluster compounds. Fundamental advances which have already been made in the theory of complex and organometallic compounds are associated with the introduction of these methods in one or other variety.[9,10,16] Since exchange-correlation effects are taken into account in the LSP method, it is not surprising that the method makes it possible to calculate fairly accurately the atomisation energies of molecules[16,17] and solids.[18]

The aim of the present review is to attempt to demonstrate, in terms of simple versions of the method of the density functional, the scope of these approximations in relation to the study of the energy characteristics of cluster compounds.

In the theoretical investigation of atomic clusters, the elucidation of a number of fundamental problems is of interest. One of these is as follows: how big must the cluster be for its electronic structure to be sufficiently close to that of the corresponding crystal? For metals, this problem has been studied within the framework of various approximate quantum-chemical methods. However, it has been found that different methods yield different results. Thus in the X_α method in terms of the scattered wave approximation (X_αSW) the similarity of a cluster to a bulky metallic specimen has been observed already when the cluster contained between 10 and 20 atoms. On the other hand, calculations based on the LCAO-MO method in terms of various approximations (EHM, CNDO, etc.) lead to the conclusion that for such small clusters the details of the electronic structure have nothing in common with metals. Thus there is as yet no unambiguous answer to the first question and the solution of the relevant problem requires both more accurate calculations, for example, within the framework of the LSP method, and experimental studies of the electronic structures of small clusters.

The second fairly important question is to what extent the bond energy in clusters varies with their size and steric structure. This question is closely related to the thermodynamic stability of clusters and their "phase" transformations for different degrees of dispersion. The knowledge of such

relations will make it possible to regulate the degree of dispersion of the given substances as a function of external conditions, which is important in various branches of chemistry. Within the framework of the one-electron method it is not possible to obtain an answer to this question because calculations of the bond energies require allowance for the correlation energy; this is extremely difficult because of the need to employ complex many-determinant wave functions, requiring an extremely long computer time for their evaluation. However, within the framework of the theory of the density functional, it is possible to answer the second question, which is discussed below in relation to carbon, sulphur, phosphorus, arsenic, and alkali metal clusters.

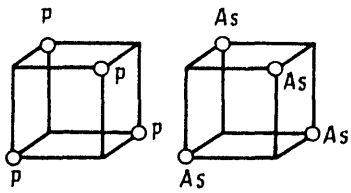


Figure 1. Tetrahedral phosphorus and arsenic clusters.

Atomic clusters can be obtained in molecular beams and also in the form of aggregates in inert matrices.[19] Fig. 1 presents phosphorus and arsenic clusters which can be detected in the gas phase at low temperatures. They have a regular tetrahedral structure. Among non-transition metals, the most unique in the sense of its capacity to produce cluster compounds is boron. Together with polyhedral clusters consisting of boron and hydrogen atoms, there exist boron clusters with beryllium, arsenic, antimony, and transition metals.

Metal clusters are obtained either in molecular beams (before the ionisation chamber of the mass spectrometer) or by condensation from the gas phase on inert supports. The latter method is most promising for the study of the properties of clusters, including their reactivity.

Metal clusters, stabilised on oxide supports, have been vigorously investigated by workers in the field of the surfaces of solids, topochemistry, and catalysis.

Atomic clusters can exist not only in the form of stable formations on the surface of a carrier but they can also be stabilised by various ligands. The simplest of these are solvates, where metallic clusters are stabilised by a ligand environment made up of solvent molecules.

The second large class of cluster compounds consists of organometallic polynuclear complexes having a central metallic nucleus with a distinct cluster structure. A modern review of the problem of the metallic bond in cluster compoounds of this kind has been published recently by Cotton and Chisholm.[20] Fig. 2 presents some examples of characteristic polynuclear cluster compounds of transition metals. According to Cotton and Chisholm,[20] transition metals can be arranged in the following sequence in terms of their ability to form metal–metal bonds in cluster compounds: Mo > Rh > Cr, Re > Tc, Ru, W, Ta, Nb > Fe, Co, Ni, Pd, Os, Ir, Pt.

One of the ways of classifying transition metal cluster compounds is on the basis of the formal oxidation state of the metal. The metal in halides and sulphides is in a high oxidation state, for example, the oxidation state of the metal is +3 in $Re_3Cl_{12}^{3-}$ and $Fe_6S_8(PR_3)_6^{2+}$, +2 in $Mo_6Cl_{14}^{2-}$, etc. There exist various cluster compounds in which the oxidation state of the metal is +1: $(\eta^5\text{-}C_5H_5)_6Ni_6\{HRh[P(OCH_3)_3]_2\}_3$, $[CH_3Rh\text{-}(cyclo\text{-}octa\text{-}1,5\text{-}diene)]_2$, and $H_6Cu_6(PR_3)_6$. A formal oxidation state of zero is observed in a large class of polynuclear metal carbonyls. Simple qualitative theories of the bond in polyhedral boranes[21] are used in calculations for certain classes of polynuclear transition metal clusters.[22] However, these theories are useful only for a formal systematic treatment of clusters and cannot be used to predict any other properties. Such studies can be regarded as a stimulus

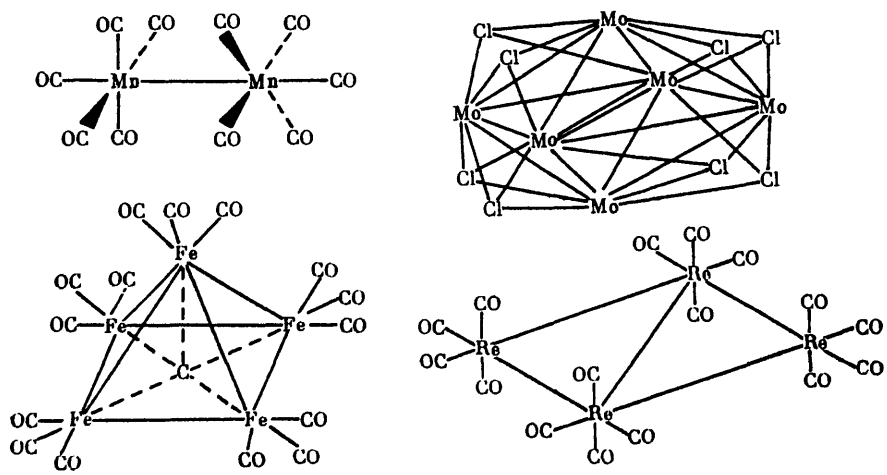


Figure 2. The most characteristic polynuclear cluster compounds.[29]

towards a more vigorous theoretical and experimental investigation of transition metal clusters in order to create a theory of this complex and interesting class of chemical compounds.

Among the simple rules obeyed by organometallic compounds, we may mention the 18-electron rule, i.e. the rule that clusters with a completely filled outer electron shell have the maximum stability.[23]

Although there are quite a few exceptions to this rule, it is useful in explaining the geometrical structural characteristics of complex organometallic compounds. This applies particularly to transition metal clusters, where simple considerations concerning hybridisation[24] or electron pair repulsion[25] are almost useless.

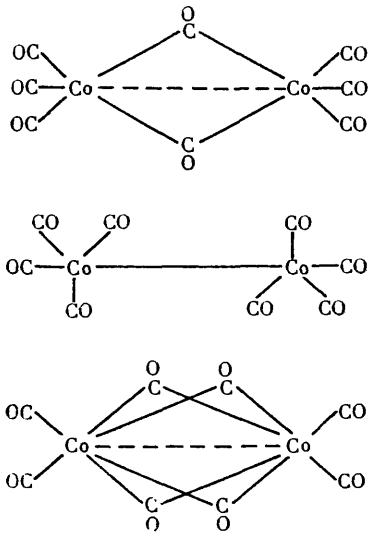


Figure 3. The structures of the dinuclear cobalt carbonyl.[26]

Many unusual structural features of metal carbonyls can be accounted for by a tendency towards the formation of an 18-electron shell. The structure of the polynuclear cobalt carbonyl $Co_2(CO)_8$ (Fig. 3*a*) can be explained from the standpoint of the formation of an 18-electron outer shell configuration. The bridging carbonyl groups form many-centre bonds and formal treatment shows that they each give up one electron to the electron shell of each cobalt atom. The diamagnetism of $Co_2(CO)_8$ indicates the formation of a Co–Co bond. Indeed the Co–Co distance is only 2.5 Å according to X-ray diffraction data.[26] It is of interest to note that in solution a second structure of the above compound (Fig. 3*b*), in which there are no bridging CO groups, coexists with that examined above;[26] this structure also satisfies the 18-electron rule. The hypothetical structure of $Co_2(CO)_8$ illustrated in Fig. 3*c* does not satisfy the 18-electron rule and, as will be shown below, is extremely unstable according to calculations by the method of the electron density functional.

Together with the 18-electron rule, analogies between the structures of cluster organometallic compounds and organopolyhedral molecules have been used in recent years. Hoffmann's principle of isolobality and the skeletal electron counting rules follow from these analogies. Since a careful review has been devoted to these questions,[27] we shall not consider them. The third type of cluster compounds (in our terminology) comprises non-classical organoelemental compounds of the type of polyhedra and *nido*-clusters. A wide variety of non-classical structures having the form of polyhedra (prismane, cubane, congressane) have been observed together with classical structures for molecules made up of carbon and hydrogen atoms only. In 1973 Bochvar and Gal'pern showed with the aid of semiempirical quantum-chemical calculations[28] that even more complex polyhedral carbon clusters can exist: a C_{20} carbododecahedron made up of 12 pentagons and a C_{60} carbo-s-eicosahedron, whose surface is made up of pentagons and hexagons alternating in an unusual manner. In these structures the carbon atoms can be linked by double bonds. Such cluster formations should be regarded as new allotropic modifications of carbon which, in contrast to the familiar graphite, diamond, and carbyne, are monomeric. Complex polyhedra made up solely of carbon and hydrogen atoms or only carbon atoms have not so far been obtained.

Extensive prospects arose in the field of the structural chemistry of polyhedral compounds after the synthesis of carbaboranes whose skeleton is made up of carbon and boron atoms. Table 1[29,30] presents typical boron clusters. A multiplicity of organometallic transition metal complexes based on carbaborane as the ligand have been obtained.[31]

Table 1. Polyhedral boron clusters.

N_a	Borane	Heteroborane	N_e	Polyhedron
4	B_4Cl_4	—	8	tetrahedron
5	$B_5H_5^{2-}$	$B_3C_2H_5$	12	trigonal bipyramid
5	$B_5H_5^{4-}$	—	14	square pyramid
6	$B_6H_6^{2-}$	$B_4C_2H_6$	14	octahedron
6	$B_6H_6^{6-}$	—	18	trigonal prism
7	$B_7H_7^{2-}$	$B_5C_2H_7$	16	pentagonal bipyramid
7	$B_7H_7^{2-}$	—	16	one-cap octahedron
8	$B_8H_8^{2-}$	$B_6C_2H_8$	18	dodecahedron
8	$B_8H_8^{2-}$	—	18	square antiprism
8	$B_8H_8^{2-}$	—	18	two-cap trigonal prism
9	$B_9H_9^{2-}$	$B_7C_2H_9$	20	three-cap trigonal prism
9	$B_9H_9^{2-}$	—	20	one-cap square antiprism
9	$B_9H_9^{4-}$	—	22	one-cap square antiprism
10	$B_{10}H_{10}^{2-}$	$B_8C_2H_{10}$	22	two-cap square antiprism
10	$B_{10}H_{10}^{2-}$	B_9H_9S	22	two-cap square antiprism
12	$B_{12}H_{12}^{2-}$	$B_{10}C_2H_{10}$	26	eicosahedron
12	$B_{12}H_{12}^{2-}$	$B_{11}PH_{12}$	26	eicosahedron
12	$B_{12}H_{12}^{2-}$	—	26	cubo-octahedron

Notation: N_a is the number of atoms in the cluster and N_e the number of skeletal electrons.

Although non-empirical calculations on clusters by the SCF LCAO-MO method are being carried out at the present time,[2] this method for the theoretical study of clusters can hardly be regarded as promising, one reason being that calculations for the cluster compounds of greatest interest from the chemical standpoint are far beyond the limits of the scope of this method.

In the calculation of the stability of the clusters, one must begin with methods in which the electronic correlation energy is taken into account sufficiently completely.[32] Within the framework of the usual non-empirical quantum-chemical methods, this is extremely difficult to achieve because even the calculation for diatomic and triatomic molecules by the configuration interaction method is extremely laborious. In this sense, it appears useful to investigate clusters within the framework of the theory of the electron density functional, which has been employed successfully for the solution of

certain physical problems.[6,14,15,33-40] This theory consists of a quantum-statistical examination of an electron liquid in which atomic nuclei "float". The energy of the ground state of a system consisting of N electrons and M nuclei with the charges z_1, z_2, ..., z_M is represented by the following electron density $\rho(\mathbf{r})$ functional:[6]

$$E[\rho] = -\sum_{\alpha=1}^{M} z_\alpha \int \rho(\mathbf{r}) |\mathbf{r} - \mathbf{R}_\alpha|^{-1} d\tau + \\ + \frac{1}{2}\iint \rho(\mathbf{r}_1)\rho(\mathbf{r}_2)|\mathbf{r}_1 - \mathbf{r}_2|^{-1} d\tau_1 d\tau_2 + \sum_{\alpha<\beta}^{M}\sum^{M} z_\alpha z_\beta |\mathbf{R}_\alpha - \mathbf{R}_\beta|^{-1} + G[\rho], \quad (1)$$

where $\mathbf{r}_i$ is the vector corresponding to the position of the ith electron, $\mathbf{R}_\alpha$ are vectors corresponding to the positions of the atomic nuclei in a three-dimensional cartesian space, and $d\tau_i = dx_i dy_i dz_i$. The functional $G[\rho]$ has not as yet been obtained in an explicit form. However, formally its form is as follows:

$$G[\rho] = \langle \Psi | \hat{T} + \hat{W} | \Psi \rangle - \frac{1}{2}\iint \rho(\mathbf{r}_1)\rho(\mathbf{r}_2)|\mathbf{r}_1 - \mathbf{r}_2|^{-1} d\tau_1 d\tau_2, \quad (2)$$

where $\hat{T}$ is the kinetic energy operator, $\hat{W}$ the interelectron interaction operator, and Ψ a many-electron wave function. The functional $G[\rho]$ includes the kinetic energy $G_t[\rho]$ and the exchange-correlation energy $G_v[\rho]$:

$$G[\rho] = G_t[\rho] + G_v[\rho]. \quad (3)$$

Approximate expressions containing several terms depending on derivatives of the electron density with respect to the coordinates x, y, and z have been found for $G_t[\rho]$ and $G_v[\rho]$ and the individual contributions have been estimated in relation to examples.[38-46] Analysis shows that exchange-correlation energy contributions close to the true values can be obtained for the potential energy with the aid of these expressions. In the case of the kinetic energy, it has been shown that the energy contributions do not decrease sufficiently rapidly as a function of the number of the term of the gradient expansion series, so that the principal inaccuracy of the method of the electron density functional is associated with the approximate form of the kinetic energy.[46] For sufficiently covalent systems, a method for the determination of the kinetic energy from the virial theorem (the virial-statistic approximation) has been recommended.[47-53]

We shall consider the question: what are the advantages of the method of the electron density functional compared with the LCAO-MO method? Firstly, the existence of a direct functional relation between the energy of the system and the electron density makes it possible to construct new and simple models of the chemical bond, which has been demonstrated in a number of studies.[47-53] Secondly, in the theory of the density functional the $3N$-variable problem, where N is the number of electrons, is replaced by a three-variable problem. This is because the exchange-correlation energy is formulated in the form of the electron density functional for the system. The development of the density functional theory has become even more crucial in recent years in connection with the development of methods for the experimental determination of the electron densities of substances.[54] Studies on the calculation of various energy characteristics of crystals from the experimental electron densities or even X-ray reflections are already being carried out.[55,56] The theory of the electron density functional is widely used in the calculations.

In view of the lack of an exact expression for the dependence of the kinetic energy functional on the electron density $G_t[\rho]$, a complete set of methods of the X_α type has been developed in the density functional theory.[9,57-61] In these methods the functional $G_t[\rho]$ is formulated as its quantum-mechanical analogue, so that the kinetic energy of the system is

$$T = \frac{1}{2}\sum_i \int \nabla\varphi_i^* \nabla\varphi_i d\tau, \quad (4)$$

where φ_i are one-particle functions and the summation is carried out over all the occupied spin-orbitals. For spin-polarised systems, the total energy can be formulated in this instance as follows:

$$E[\varphi_{i\alpha}, \varphi_{i\beta}] = -\sum_{\alpha=1}^{M} z_\alpha \int \rho(\mathbf{r})|\mathbf{r} - \mathbf{R}_\alpha|^{-1} d\tau + \\ + \frac{1}{2}\iint \rho(\mathbf{r}_1)\rho(\mathbf{r}_2)|\mathbf{r}_1 - \mathbf{r}_2|^{-1} d\tau_1 d\tau_2 + \sum_{\alpha<\beta}^{M}\sum^{M} z_\alpha z_\beta |\mathbf{R}_\alpha - \\ - \mathbf{R}_\beta|^{-1} + \frac{1}{2}\sum_i^{k_\alpha} \int \nabla\varphi_{i\alpha}^* \nabla\varphi_{i\alpha} d\tau + \frac{1}{2}\sum_i^{k_\beta} \int \nabla\varphi_{i\beta}^* \nabla\varphi_{i\beta} d\tau + G_v[\rho_\alpha, \rho_\beta], \quad (5)$$

where ρ_α and ρ_β are the electron densities due to electrons with the spins α and β respectively and

$$\rho_\sigma = \sum_i^{k_\sigma} \varphi_{i\sigma}^* \varphi_{i\sigma}, \quad (6)$$

Where $\varphi_{i\sigma}$ is the spin-orbital wave function for the spin σ and k_σ the number of occupied orbitals for the spin σ. By varying the energy with respect to $\phi_{i\sigma}$, we obtain an equation of the Hartree–Fock type taking into account the exchange-correlation energy determined by the functional $G_v[\rho_\alpha, \rho_\beta]$:

$$\left[-\frac{1}{2}\Delta - \sum_\alpha z_\alpha |\mathbf{r} - \mathbf{R}_\alpha|^{-1} + \int \rho(\mathbf{r}')|\mathbf{r} - \mathbf{r}'|^{-1} d\tau' + \right. \\ \left. + \frac{\delta G[\rho_\alpha, \rho_\beta]}{\delta \rho_\sigma}\right] \varphi_{k\sigma} = \varepsilon_{k\sigma}\varphi_{k\sigma}. \quad (7)$$

The expression for the exchange-correlation potential

$$V_{ex,c}[\rho_\alpha, \rho_\beta] = \frac{\delta G[\rho_\alpha, \rho_\beta]}{\delta \rho_\sigma} \quad (8)$$

has a different form in different versions of this method. For example, the following expression is used in the X_α approximation:

$$V_{X_\alpha} = \frac{9\alpha}{2}\left[\frac{3}{4\pi}\rho(\mathbf{r})\right]^{1/3}. \quad (9)$$

The advantages and disadvantages of the potential defined by Eqn. (9) in the X_αSW method, applied to calculations on clusters, chemisorption, and catalysis, have been frequently discussed in the literature.[57-59] Although the known successes of the X_αSW method in calculations on the clusters give rise to some hope, the difficulties due to the arbitrary selection of the atomic sphere radii as well as those in the interpretation of the results engender some scepticism.[62] Other versions of methods of the X_α type, which are the discrete variation method[10-12] and the LSP method,[13,14,16] are free from the disadvantages of the X_αSW method. An appreciable advantage of these procedures is the possibility of using any system of basis functions, including atomic functions, which brings these methods closer to the SCF LCAO-MO procedure.

Certain examples of the employment of simple versions of the theory of the electron density functional for the calculation of the energy characteristics of clusters are presented below and the question of the variation of the bond energy in homoatomic clusters as a function of their size and steric structure is examined.

II. THE ELECTRONIC STRUCTURE AND ENERGY CHARACTERISTICS OF ATOMIC CLUSTERS

In their review Kuz'minskii and Bagatur'yants[2] give a good selection of theoretical studies on the calculation of the electronic structures of metal clusters (mainly the semiempirical EHM, CNDO, etc. methods). The following groups have been examined:

(a) alkali metals (Li_2, Li_3, Li_4, Li_5, Li_6, Li_7, Li_8, Li_9, Li_{10}, Li_{13}, Na_2, Na_3, Na_4, Na_8, K_2, K_3);

(b) alkaline earth metals (Be_2, Be_4, Mg_2, Ca_2, Sr_2, Ba_2);

(c) aluminium group metals (Al_2, Al_5, Al_9, Al_{13}, Al_{19}, Al_{25}, Al_{43}, Al_{59}, Ga_2, In_2, Tl_2);

(d) heavy elements (Sn_2, Pb_2, Bi_2);

(e) noble metals and Group IIB metals (Cu_2, Cu_3, Cu_4, Cu_5, Cu_6, Cu_8, Cu_9, Cu_{10}, Cu_{13}, Cu_{16}, Cu_{19}, Cu_{31}, Cu_{39}, Cu_{43}, Ag_2, Ag_6, Ag_7, Ag_8, Ag_{10}, Ag_{13}, Ag_{19}, Ag_{43}, Ag_{55}, Au_2, Au_6^{2+}, Au_9^{3+}, Au_{11}^{3+}, Zn_2, Cd_2, Cd_{28});

(f) transition metals (Ti_2, Ti_3, Ti_4, Ti_5, Ti_6, V_2, Cr_2, Cr_3, Cr_4, Cr_5, Cr_6, Mn_2, Mn_{13}, Fe_2, Fe_3, Fe_4, Fe_5, Fe_6, Fe_9, Fe_{15}, Co_2, Ni_2, Ni_3, Ni_4, Ni_5, Ni_6, Ni_9, Ni_{13}, Ni_{14}, Pd_2, Pd_{12}, Pd_{19}, W_9, Pt_{13}).

Together with the homoatomic clusters, the above review[2] also quotes the results of calculations (mainly by semiempirical methods) on bimetallic heteroatomic clusters and clusters on a support.

A simple non-empirical version of the theory of the density functional, namely the virial-statistical approximation, has been used[63] to investigate the clusters. In this approximation the kinetic energy is determined from the relation between the virial theorem for the equilibrium interatomic distances in the cluster:

$$T[\rho] = -\frac{1}{2}V[\rho]. \qquad (10)$$

The total energy is then defined by the following formula:

$$E[\rho] = \frac{1}{2}V[\rho]. \qquad (11)$$

The sum of the atomic densities

$$\rho(\mathbf{r}) = \sum_{\alpha}\rho_{\alpha}(\mathbf{r}), \qquad (12)$$

where $\rho_\alpha(\mathbf{r})$ are the Hartree–Fock electron densities of the corresponding atoms α in a free state, was selected in this instance as the approximation for electron density for homoatomic systems. In the simple statistical theory (the TFD equation), Eqn.(12) for the electron density in a homoatomic molecule is fairly rigorous, which has been noted in the studies of Firsov[64] and (later) Slater.[65] Slater notes that the practical experience gained in X_α calculations has shown that Eqn.(12) for the density of the homoatomic molecules is a fairly satisfactory approximation. Analysis of non-empirical calculations[66,67] has also shown that the formation of homoatomic molecules from atoms does not entail a significant redistribution of electron density (the H_2 molecule is an exception).

The bond energies in homonuclear diatomic molecules made up of the atoms of non-transition elements ranging from Li_2 to Bi_2, calculated in terms of the virial-statistical approximation, are compared in Fig. 4 with the experimental values.[68] The atomic electron densities for the ground state in terms of a one-exponential basis set of the Slater type were used in the calculation. In the evaluation of the bond energy no adjustable parameters were employed and account was taken of all the electron shells of the atoms, both valence and skeletal. The distances between the atoms in the diatomic molecules were assumed to be equal to the experimental values.[68] In those cases where the experimental interatomic distances are not available, they were estimated from the formula

$$R(\text{Å}) = 0.3500 + 1.6072\, r_M, \qquad (13)$$

where r_M are the atomic radii of the elements.[69,70]

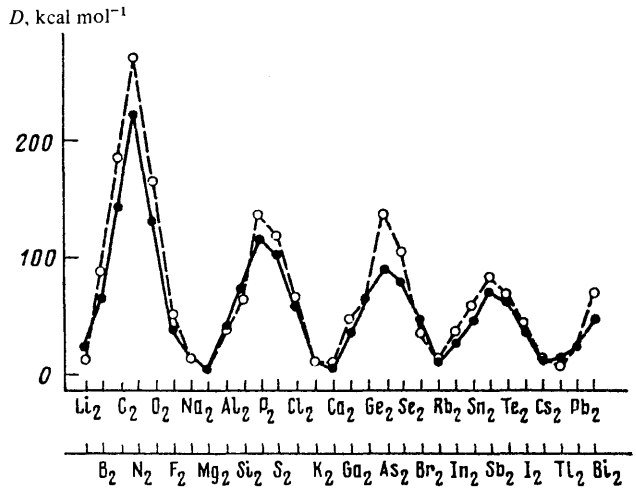


Figure 4. Comparison of the experimental (continuous line) and calculated (dashed line) bond energies in diatomic homonuclear molecules of non-transition elements.[63]

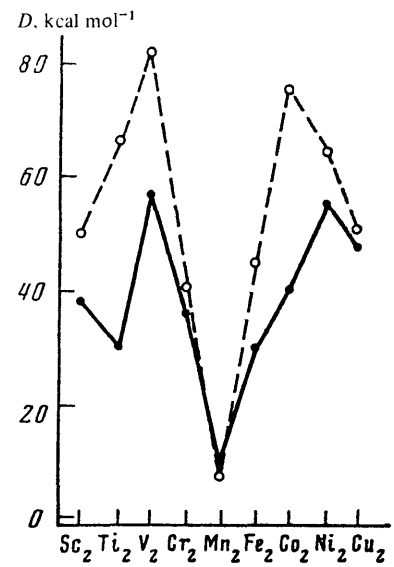


Figure 5. Comparison of the experimental (continuous line) and calculated (dashed line) bond energies in diatomic homonuclear molecules of the elements in the Fourth Period in Mendeleev's Table.[71]

A distinct qualitative agreement between the results of the calculations and the experimental data is observed. It is noteworthy that the non-empirical SCF LCAO-MO method,

which takes into account the electron correlation energy to only an insignificant extent, does not yield even a qualitatively correct picture of the changes in bond energy. In particular, for the fluorine molecule the SCF LCAO-MO calculation does not produce even a positive bond energy. The analogous relations for diatomic gas-phase molecules of the transition metals in the Fourth Period are presented in Fig. 5.[71]

The method described above has been used[63] to calculate the bond energies in the gas-phase sulphur molecules polymerised to different extents. Clusters having the compositions S_4, S_5, S_6, S_7, S_8, S_9, S_{10}, S_{11}, and S_{18} were examined. The geometrical parameters used in the calculations were taken from a theoretical calculation by the method of molecular dynamics.[72] This choice of molecular geometry is dictated by the fact that the experimental studies of S_N structures have been carried out only for a small class of compounds and their results are frequently contradictory. The calculated bond energies, evaluated per sulphur atom, for different molecules and the available experimental data are compared in Table 2. The calculations showed that the S_8 cluster in the form of a ring has the most stable configuration. It is known that orthorhombic crystalline sulphur, in which layers of cyclic S_8 molecules are stacked,[73] is thermodynamically stable. Table 2 also yields the results of calculations on diatomic molecules and tetrahedral clusters of phosphorus and arsenic (Fig. 1);[63] the calculated bond energies per atom have been compared with experimental values.[68] In agreement with the experiment, the calculation shows that the tetrahedral P_4 and As_4 clusters are more stable at low temperatures than the diatomic molecules.

Table 2. Comparison of the calculated and experimental bond energies D of sulphur, phosphorus, and arsenic molecules*.

System	D_{theor}/N, kcal mol^{-1}	D_{exp}/N, kcal mol^{-1}	System	D_{theor}/N, kcal mol^{-1}	D_{exp}/N, kcal mol^{-1}
S_4	66.2	55.94	S_{10}	75.1	—
S_5	71.6	60.43	S_{11}	74.0	—
S_6	72.2	61.60	S_{18}	73.8	—
S_7(Cs)	73.7	61.78	P_2	67.2	58.0
S_7(C_2)	74.8	—	P_4	83.5	71.9
S_8	85.3	62.62	As_2	57.9	45.5
S_9	71.8	—	As_4	73.7	63.3

*Here and henceforth D/N is the bond energy calculated per atom.

Two allotropic forms of carbon, namely graphite and diamond, for which there also exist submodifications involving a change in long-range order, were known previously. In 1978 Korshak et al.[74] discovered carbyne—the third form of carbon, consisting of filamental polymers made up of carbon atoms only. A series of quantum-chemical studies of the character of the bond in carbyne (see, for example, Stankevich and Tomilin[75]) have been carried out. It has been shown that the bonds in carbyne can alternate. Calculations have been made[63] for clusters of three allotropic forms of a carbon—graphite, diamond, and α-carbyne. Fig. 6 presents the calculated dependence of the bond energy per carbon atom on the size of the carbon cluster. The horizontal lines indicate the corresponding bond energy for crystals obtained in terms of the same approximations as those employed in the calculations on the clusters.[76] It is seen from Fig. 6 that the calculated stability series for the three allotropic forms of the carbon crystal agrees qualitatively with experiment: graphite > diamond > carbyne. When carbon clusters containing less than 20 atoms are examined, the stability series is different than for crystals: carbyne > graphite > diamond. When the number of atoms in the cluster is more than 20, a change in the above sequence takes place—curves *1* and *3* intersect (graphite > carbyne > diamond). It is seen from these calculations that, depending on the size of the clusters, the energy relations between different modifications vary. Analysis of the curves for the C_N clusters with $N \leq 50$ and data for crystals gives rise to the hypothesis that, for certain finite dimensions of the clusters, curves *2* and *3*, corresponding to diamond and carbyne, should intersect. On this basis, one may conclude that the carbyne molecule is thermodynamically stable only for a finite chain length. On further increase of its size, it should be converted into a more stable form, for example into a structure with cross-links between the polymer chains.

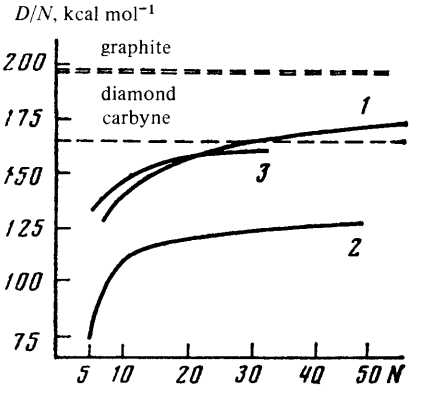


Figure 6. Dependence of the bond energies calculated per atom on the size of carbon clusters: 1) graphite; 2) diamond; 3) carbyne.[63]

Certain hypothetical carbon systems, which are formed as a result of the appearance of regular cross-links between the carbon chain macromolecules, having fourfold screw symmetry axes have been proposed.[77] In one of the hypothetical structures (I) each chain is surrounded by four chains of the same chirality ($I4_132$ symmetry group, identical lengths of all the bonds), while in another structure (II) each chain is surrounded by four chains of opposite chirality ($I\bar{4}m2$ symmetry group, the geometry is described in terms of two parameters: the bond length r_1 between neighbouring atoms in different chains and the bond length r_2 between neighbouring atoms in the same chain with $r_1 < r_2$).

Calculations have been made[78] of the bond energies for six crystalline modifications of carbon: graphite, diamond, α-carbyne, β-carbyne, and the two hypothetical systems (I) and (II). The results of these calculations are presented in Table 3. Evidently the hypothetical modification (I) is much more stable than the carbyne structures (α and β).

The different types of behaviour of the bond energy in carbon clusters as a function of their size for different allotropic forms are caused primarily by the different degrees of unsaturation of the bonds in the clusters. Diamond is a

three-dimensional crystal, graphite is close to a two-dimensional crystal, while carbyne is close to a one-dimensional crystal.

Table 3. The relative energies ΔE of various forms of carbon.[78]

Modification	ΔE, kcal mol^{-1}	Modification	ΔE, kcal mol^{-1}
Graphite	0.0	(II)	32.5
Diamond	1.5	β-Carbyne	33.0
(I)	7.4	α-Carbyne	32.8

The main conclusion which can be reached on the basis of the calculations for the carbon clusters is as follows: the energies of the "phase" transformations of the carbon clusters depend significantly on their dimensions, varying not only in absolute magnitude but also in sign. The question arises of the size of the cluster up to which one can speak of changes in its state of aggregation or a phase transition. Computer experiments performed for systems with a Lennard-Jones interaction potential have shown that phase transitions are observed for clusters consisting of ten particles.[79]

The dependence of the bond energy on the size of the cluster has been studied in greatest detail for alkali metals, particularly lithium. A scheme describing the growth of the lithium crystal has been proposed[80] on the basis of non-empirical calculations. It is noteworthy that the bond energies calculated in the above study[80] per atom for structures most favoured by energy factors increase monotonically for small dimensions of the clusters ($N \leq 5$) and then remain approximately constant at 9–12 kcal mol^{-1} (as N varies from 5 to 13).

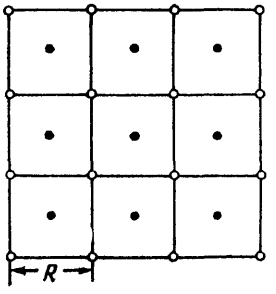


Figure 7. The geometrical structure of lithium clusters.[81]

Within the framework of the method of the gradient expansion of the energy, a study has been made[81] of the variation of the equilibrium distances and bond energies per atom for clusters of the type Li_N with N varying from 9 to 100. These are apparently the largest clusters for which theoretical calculations have been made (disregarding clusters in systems with a simple interaction potential of the Lennard-Jones type). It is noteworthy that, in contrast to the study of Fantucci and Balzarini,[80] Borisov[81] carried out a calculation for a fixed spatial symmetry of the clusters. Fig. 7 illustrates the geometrical structure of lithium clusters for the body-centred cubic lattice used in Borisov's calculations on clusters.[81] The cluster is made up of two types of layers: a layer of type L_1, designated by filled circles and containing 9 lithium atoms, and a layer of type L_2, designated by open circles and containing 16 lithium atoms. The distance between the layers is $R/2$, where R corresponds to the closest Li–Li distance within the limits of one layer. For example, the Li_{50} cluster consits of four layers: $L_1L_2L_1L_2$.

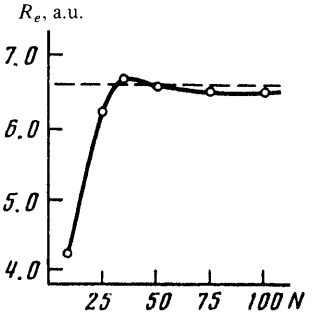


Figure 8. Dependence of the equilibrium Li–Li distance in the Li_N clusters on N.[81]

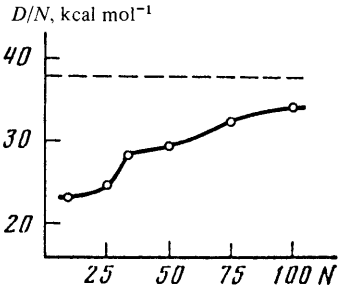


Figure 9. Dependence of the bond energy calculated per atom on the size of the lithium clusters.[81]

The energy of the Li_N clusters was optimised for each cluster with respect to the distance R. Fig. 8 illustrates the calculated dependence of the equilibrium distance R_e (in a.u.) in the Li_N clusters on N for a body-centred cubic structure. The dashed line corresponds to the experimental equilibrium distance R_e for a lithium crystal with a body-centred cubic lattice. Fig. 8 shows that, for low values of N, a marked dependence of R_e on the size of the clusters is observed. For clusters containing 34 lithium atoms, there is virtually no dependence of R_e on N. Fig. 9 presents the dependence of the bond energy per atom on the size of the Li_N clusters. The curve illustrated has a lower slope than the $R_e(N)$ curve and approaches fairly closely the corresponding experimental value for the crystal listed in Table 4.[76] The calculated bond energies have been compared with the available experimental

values.[68] Calculations for the Li_{50} clusters[81] in the body- and face-centred structures have shown that the latter structure is more favourable as regards energy, the difference between the energies amounting to 1.8 kcal mol^{-1}. For comparison, one may note that the corresponding difference for crystals is 0.3 kcal mol^{-1} (Table 4)[76] and the experimental difference is 0.49 kcal mol^{-1}.[82] Consequently the energy of the fcc → bcc "phase" transformation in the lithium clusters decreases with increase in the size of the cluster but does not change sign (in contrast to the transformations in the graphite–diamond–carbyne carbon system).

Table 4. The results of calculations for alkali metal crystals.[76]

Metal	Structure	$-E_{theor}$, a.u.	D_{theor}, kcal mol^{-1}	D_{exp}, kcal mol^{-1}
Li	hex.	7.4120	47.9	—
Li	BCC	7.4114	47.5	37.7
Li	FCC	7.4119	47.8	—
Na	BCC	158.4455	30.4	25.8
Na	FCC	158.4460	30.7	—
K	BCC	581.8500	31.3	21.5
Rb	BCC	2839.9763	22.6	19.6

Notation: E is the total energy of the crystal, hex. a hexagonal lattice, BCC a body-centred cubic lattice, and FCC a face-centred cubic lattice.

III. STABILITY OF ORGANOELEMENTAL CLUSTERS

So far few studies have been published on the calculation of the electronic properties of organometallic polynuclear clusters. Only calculations for individual cluster compounds can be encountered in the literature. The most general question for organometallic clusters is that of the character of the metal–metal bond, which has been discussed in a series of reviews (see, for example, Cotton and Chisholm.[20] The fact that the shortest distances are observed in complexes with bridging ligands has attracted attention in the analysis of the interatomic metal–metal distances in homopolymetallic π-complexes.[83] However, certain calculations have shown that the metal–metal bond is absent precisely in compounds of this type and the cluster is stabilised by interactions via bridges. Thus non-empirical calculations have been performed[84] for two cluster complexes: $Fe_3(CO)_{12}$ and $[C_5H_5Fe(CO)_2]_2$. Fig. 10 illustrates schematically the structures of these clusters. In the $Fe_3(CO)_{12}$ complex (Fig. 10a) and Fe(1) and Fe(2) atoms are joined via two bridging CO groups. Analysis of the occupied molecular orbitals (MO) has shown that there are no MO in which there is a linkage between the d orbitals of the Fe atoms. An analogous picture has been observed for the $[C_5H_5Fe(CO)_2]_2$ complex illustrated in Fig. 10b. Thus, despite the short M–M interatomic distances, there is no direct interaction between the metal atoms in the complexes indicated.

Calculations for the dinuclear nickel complex $(\eta^5\text{-}C_5H_5Ni)_2 . C_2H_2$ have confirmed the existence of a single σ-bond between the nickel atoms. Calculations for the $M_2Cl_4(PR_3)_4$ (M = Mo or W) complexes by the X_αSW method have been carried out in a recent study[86] (Fig. 11). They showed that the M–M bond in these complexes is quadruple and that the bonding molecular orbitals are of the σ, π, and δ types. The calculated[86] electronic transition energies have been fully confirmed by experiment (photoelectron spectroscopy). Thus the multiplicities of the M–M bonds in transition metal cluster compounds can vary from zero to four.

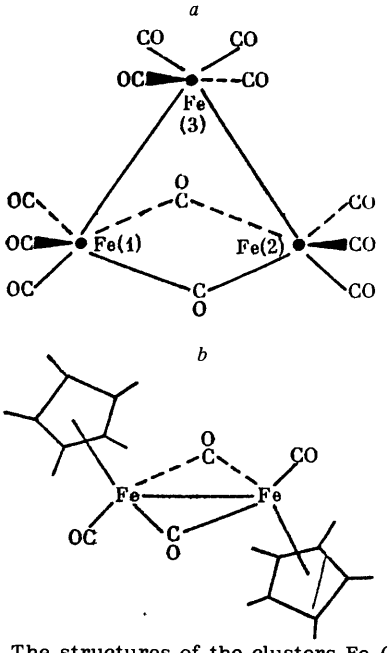


Figure 10. The structures of the clusters $Fe_3(CO)_{12}$ (*a*), $[C_5H_5Fe(CO)_2]_2$ (*b*).[84]

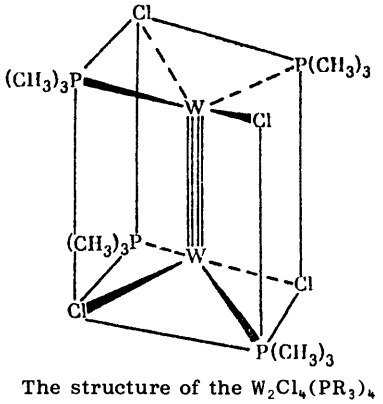


Figure 11. The structure of the $W_2Cl_4(PR_3)_4$ cluster.[86]

The study of the $Co_2(CO)_9$ cluster by various physical methods (infrared spectroscopy and X-ray diffraction)[26] showed that the compound has different structures under different conditions. According to the results of X-ray diffraction analysis,[26] the $Co_2(CO)_8$ solid phase has a structure with two C = O bridge bonds (Fig. 3*a*). In solution form (II) (Fig. 3*b*) coexists with this structure [form (I)], and the ratio of these forms can vary as a function of temperature. Whereas form (I) predominates at low temperatures, at room

temperature the concentration of form (II) is ~50%. Calculations of the atomisation energies for three structures of the dinuclear cobalt carbonyl have been carried out.[71] Structure (III), illustrated in Fig. 3*a* is hypothetical and no evidence for its existence has been obtained. Calculations have shown that stability decreases in the following sequence of structures: (I) > (II) > (III). Structure (III) proved to be least favourable on energy grounds and is hardly likely to exist. As mentioned above, the 18-electron rule also does not hold for this structure. The ease of the interconversion of structures (I) and (II) is indicated by purely chemical investigations. A study of the reaction involving the exchange of CO groups showed that all eight CO groups of the complex can be readily exchanged. Apparently equilibrium is established during the exchange reaction between forms (I) and (II) of the dinuclear cobalt carbonyl.[26]

Table 5. Certain characteristics of transition metal clusters.

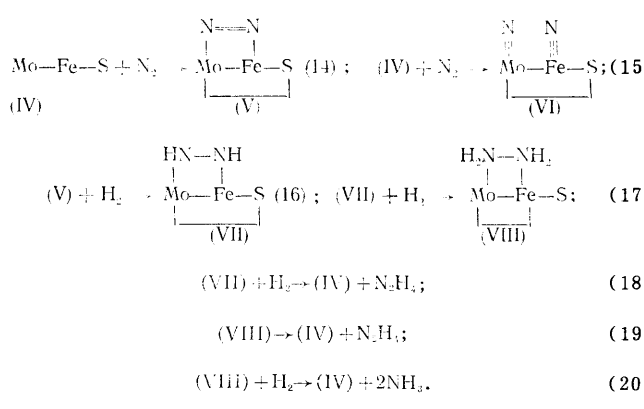
Geometry	N	n_u	n_c	Cluster
Monomer	1	0	9	$Ni(CO)_4$
Dimer	2	1	17	$Fe_2(CO)_9$
Trimer	3	3	24	$Os_3(CO)_{12}$
Tetrahedron	4	6	30	$Rh_4(CO)_{12}$
"Butterfly"	4	5	31	$Re_4(CO)_{16}^{2-}$
Planar square	4	4	32	$Pt_4(O_2CCH_3)_8$
Trigonal bipyramid	5	9	36	$Os_5(CO)_{16}$
Square pyramid	5	8	37	$Fe_5(CO)_{15}C$
Two-cap tetrahedron	6	12	42	$Os_6(CO)_{18}$
Octahedron	6	11	43	$Rh_6(CO)_{16}C$
One-cap square pyramid	6	11	43	$Os_6(CO)_{18}H_2$
Corner-linked bitetrahedron	6	11	43	—
Pentagonal pyramid	6	10	44	—
Trigonal prism	6	9	45	$Rh_6(CO)_{15}C$
One-cap octahedron	7	14	49	$Rh_7(CO)_{16}^{3-}$
One-cap trigonal prism	7	12	51	—
Two-cap octahedron	8	17	56	—
Square antiprism	8	15	57	$Co_8(CO)_{20}C^{2-}$
Two-cap trigonal prism	8	15	57	—
Cube	8	12	60	$Ni_8(PC_6H_5)_6(CO)_8$
Three-cap octahedron	9	18	63	—
Three-cap trigonal prism	9	17	64	—
One-cap square antiprism	9	16	65	—
One-cap cube	9	15	66	—
Two-cap cube	10	19	71	—
Two-cap square antiprism	10	19	71	—
Three-cap trigonal bypyramid	12	28	80	—
Eicosahedron	12	23	85	—
Three-cap hexagonal bipyramid	13	32	85	$Rh_{13}(CO)_{24}H_3^{2-}$
Face-centred cube	14	36	90	—

Notation: N is the number of atoms in the cluster, n_u the number of unoccupied orbitals, and n_c the number of cluster bond orbitals.

Whereas the structure of $Co_2(CO)_8$ most favoured by energy factors has bridge bonds, a direct M–M bond has been observed in the dinuclear manganese and technetium carbonyls. The energies of the M–M bond in the dinuclear $Mn_2(CO)_{10}$ and $Tc_2(CO)_{10}$ clusters have been estimated[87] within the framework of the virial-statistical approximation:[48,49] 52 and 100 kcal mol^{-1} have been obtained for $Mn_2(CO)_{10}$ and $Tc_2(CO)_{10}$ respectively, which exceeds the experimental values by a factor of approximately 2. Such unduly high calculated bond energies are apparently associated with the fact that no account had been taken of the relaxation of the bonds remaining after the rupture of the metallic bond. Thus the calculation and experiments showed that the bond strength increases on passing to heavier elements in the Periodic Table. This is a general phenomenon due to the increase of the degree of overlap of the atomic orbitals of the heavier elements and explains the increased ability of heavy transition metals to produce polynuclear carbonyl complexes.

There are as yet no quantitative theories of the dependence of the ability to form cluster compounds on the nature of the metal. However, qualitative aspects have been discussed[22] and have been justified by EHM calculations. The molecular orbitals of a cluster formed by transition metals can be divided into two classes: the unoccupied antibonding orbitals (UAO) and cluster valence orbitals (CVO). Only the CVO are suitable in terms of energy for combining with ligands and for ensuring the stability of the metallic skeleton of the cluster. Table 5[22] lists certain characteristics of transition metal clusters; it also includes examples of stable clusters corresponding to specified values of N, a specified geometry, and a specified number of valence electron n_k in the cluster valence orbitals. The n_k-electron rules are in fact extensions of the 18-electron rule to mononuclear transition metal complexes ($n_k = 18$ for $N = 1$).

It is known that metal clusters can behave as catalytic centres in various chemical reactions.[29] A simplified mechanism of the binding of nitrogen on the Mo–Fe–S model cluster, to which an important role has been attributed in the biological fixation of nitrogen, has been examined.[71] A scheme for the hydrogenation of nitrogen on the Mo–Fe–S dinuclear cluster, which is similar to that proposed by Likhtenshtein and Shilov for the catalytic hydrogenation of nitrogen in the presence of complex homogeneous catalysts, is presented below:[88]



(18)

(19)

(20)

The atomisation energies of the intermediate forms (V)–(VIII) have been calculated. The bond lengths and angles have been taken from Hardy et al.[89] and the missing interatomic distances have been determined as the sums of the covalent atomic radii.

Table 6 lists the calculated heats Q of individual stages of the reaction. Only a qualitative comparison of the heats Q is possible, because, apart from the roughness of the approximations, no account has been taken in the calculation of effects such as the influence of the protein component of the nitrogenase molecule, the pH of the medium, temperature, etc. It follows from the calculations that stage (15) is very highly endothermic. It is therefore possible to reject immediately the nitride mechanism of nitrogen fixation. In the hydrazine mechanism stage (16) is slowest and results in the formation of diimide coordinated to the catalyst. In order to estimate approximately the activation energies for the individual stages in the hydrogenation of nitrogen, we shall make use of the Brønsted–Semenov relation between the activation energy and the heat of reaction:

$$E_{act} = A_0 + 0.75\,|Q| \qquad (21)$$

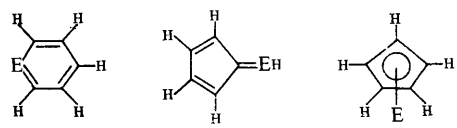
$$E_{act} = A_0 - 0.25\,|Q| \qquad (22)$$

for the endothermic and exothermic reactions respectively. Assuming that stage (14) takes place without an activation energy (this hypothesis does not alter the qualitative conclusions), we shall determine the unknown value of A_0 from Eqn.(22). Assuming further that A_0 does not change on passing from one stage to another (for radical reactions, this approximation holds[90]), the activation energies E_{act} were calculated for all the intermediate stages of the nitrogen hydrogenation reaction (Table 6). Comparison of the activation energies for the individual stages leads to the following probable pathway in the nitrogen hydrogenation reaction: (14) → (16) → (17) → (20). It was found that this pathway leads to the reduction of nitrogen to ammonia. The formation of less reduced forms is energetically unfavourable, in agreement with experiment.

Table 6. The calculated values of Q and E_{act} (kcal mol^{-1}).[71]

Stage	(14)	(15)	(16)	(17)	(18)	(19)	(20)
Q	31.5	−94.1	−50.4	18.9	0.0	−18.9	25.2
E_{act}	0.0	—	45.5	3.5	8.0	12.5	2.0

The mass spectra of π-cyclopentadienyliron carbonyl complexes π-$C_5H_5Fe(CO)_2ER_3$ containing an Fe–E bond, where E is a Group IV element (E = Si, Ge, Sn, or Pb) show intense peaks due to the $C_5H_5E^+$ ions whose intensity is sometimes a maximum.[91–96] They arise as a result of a complex rearrangement from molecular or decarbonylated ions $C_5H_5FeER_3$ (R = alkyl or halogen). This rearrangement takes place with the simultaneous involvement of at least nine bonds and has a very low activation energy. The unusually high intensity of the peaks due to the $C_5H_5E^+$ ions indicates their high stability. It is possible to put forward three possible structures of this ion, namely the elementophenyl (a), the elementofulvenyl (b), or the *nido*-cluster (c):



a *b* *c*

A calculation[97] of the atomisation energies of these structures of the $C_5H_5Ge^+$ ions showed that the structure of the *nido*-cluster has the highest stability. Similar calculations were later performed[98] for all the Group IV elements and it was shown that in all cases the cluster ions are more stable than the isomeric elementophenyl and elementofulvenyl ions and that their stability increases on passing from lead to carbon. The conclusion that the *nido*-cluster has the highest stability agrees with non-empirical calculations for $C_5H_5Si^+$ [99] and semiempirical calculations for the $C_5H_5Si^+$ and $C_5H_5C^+$ ions.[100] It is noteworthy that the predicted[97] stability of the *nido*-cluster of germanium has been confirmed by the synthesis of a compound containing this ion in the form of a *nido*-cluster.[101,102]

Calculations have been performed[103] by the SCF LCAO-MO method in the CNDO/2 approximation for the *nido*-clusters $C_5H_5E^q$, where E are the elements of the First and Second Periods (from H to Ne) and q assumes values of +1, 0, and −1. It was found that the stability of the *nido*-clusters increases with increase of the nuclear charge of the atom E, reaches a maximum, and then again falls towards the end of the Second Period. The $CpBe^-$, CpB, and CpC^+ clusters, in which the eight-electron shell is formally filled, show the highest stability under these conditions. Together with the $Me_5C_5Sn^+$ and $Me_5C_5Ge^+$ *nido*-clusters,[101,102] there exist stable molecules of the semi-sandwich type with an eight-electron shell, namely CpIn and CpTe.[104] On the basis of the results of an investigation,[103] it is possible to put forward the existence of the following *nido*-cluster: CpE^+ (E = C, Si, or Pb), CpE (E = B, Al, or Ga), and CpE^- (E = Be or Mg).

The numerous calculations for clusters of three types ("isolated" homoatomic, polynuclear organometallic, and *nido*-clusters) examined above show that the method of the electron density functional makes it possible to solve many interesting problems involving the energy relations of clusters even in its simple versions. Hitherto these simple versions have been applied to fairly covalent clusters, for which it is possible to neglect the charge transfer between the atoms (or ions). This is because the electron density of the system can be approximated by the sum of the electron densities of the free atoms (or ions).

In the future the method of the electron density functional can develop in two directions when applied to cluster theory: (1) with allowance for charge transfer between the atoms (or ions) by including the corresponding variational parameters in the electron density function, as, for example, has been done by Borisov;[46] (2) with analysis of the experimental electron densities to obtain an approximation to $\rho(\mathbf{r})$ in energy calculations, as has been done for crystals.[55,56] These improvements will naturally lead to certain complications in the calculations but the latter will nevertheless be much simpler than the calculations by the traditional quantum-chemical methods of the type of SCF LCAO-MO. Together with this, one-electron approaches based on the formal treatment of Kohn and Sham,[15] where the electron correlation is taken into account in the form of the electron density functional, show much promise for the calculation of the electronic structures of cluster compounds.

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The Chemistry of the Cluster Compounds of Technetium

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The results of studies published up to 1983 inclusive and devoted to the synthesis and the molecular and electronic structure as well as the chemical and physicochemical properties of dinuclear and polynuclear cluster compounds of technetium are examined. It is shown that the majority of the chemical and physicochemical properties of such cluster compounds are analogous to those of the similar compounds of other *d* transition elements. However, a number of properties of the technetium cluster differ from those of other transition elements, which is explained from the standpoint of modern theoretical concepts. The bibliography includes 106 references.

CONTENTS

I. Introduction 373
II. Synthesis and molecular and electronic structures 373
III. Chemical properties in solutions 388
IV. Thermochemical behaviour 391

I. INTRODUCTION

Technetium,[1] which is a typical representative of *d* transition elements of the second transition series, has properties most of which are similar to those of rhenium and in certain cases molybdenum. Since it is known[2-4] that the maximum capacity of transition elements for cluster formation with weak-field ligands is manifested by Group VI and VII elements, technetium is included among the most powerful cluster-forming elements. However, only the one anion $[Tc_2Cl_8]^{3-}$, in which a powerful metal–metal bond (M–M) is manifested, was known for technetium for a long time. The absence of data for this field of the chemistry of cluster compounds was due primarily to the low availability of technetium and its radioactivity.

Complexes of technetium in the lowest oxidation states are unstable and are formed as a rule with strong-field ligands, while complexes with weak-field ligands exist only in the presence of metal–metal bonds.[1] Thus the chemistry of complexes of technetium in oxidation states below 3+ with weak-field ligands can be regarded in essence as the chemistry of the cluster compounds of this element.

The studies on the chemistry of cluster compounds of technetium in the USSR were initiated at the beginning of the 1970's at the Institute of Physical Chemistry of the USSR Academy of Sciences after weighable amounts of this element had been obtained from the waste in the processing of nuclear fuel from atomic reactors.[1] This review deals with the present state of the chemistry of the cluster compounds of technetium and surveys and analyses the results of studies of the molecular and electronic structures of dinuclear and polynuclear technetium complexes with metal–metal bonds. Much attention is devoted to questions of the synthesis of cluster compounds of technetium and the investigation of their chemical and physicochemical properties.

II. SYNTHESIS AND MOLECULAR AND ELECTRONIC STRUCTURE

It is possible to differentiate two methods of synthesis of cluster compounds of technetium with weak-field ligands. The first[5] consists in the reduction of pertechnetate ions in concentrated hydrochloric acid by metallic zinc. The other method of synthesis, which has been used by the authors of this review,[6-8] is based on the reduction of pertechnetate ions by molecular hydrogen under pressure in an autoclave. This method has the advantage that the crystals produced are well formed and contain no extraneous impurities. The autoclave method had been developed initially for the synthesis of dinuclear technetium clusters with the $[Tc_2Cl_8]^{3-}$ anions and inorganic and organic cations.[6-8] Subsequently the autoclave method for the synthesis of clusters proved convenient also for the synthesis of more complex technetium clusters, including polynuclear clusters.[9-13] All the technetium clusters known at present can be divided arbitrarily into groups characterised by similar molecular and electronic structures.

1. Dinuclear Cluster Compounds of Technetium with the d^4–d^5 Electronic Configuration of the Central Atoms

These compounds constitute the most numerous groups of technetium clusters which have been investigated (Table 1, compounds 8–22). In our view this is due to the greater stability of the d^4–d^5 clusters compared with the d^4–d^4 clusters and also the fact that compounds with the $[Tc_2Cl_8]^{3-}$ anions had been obtained initially for technetium[5-8,14-16] and were subsequently employed to synthesise new technetium clusters.[9-13,17,18]

(a) *The Octachloroditechnetates* $M_3[Tc_2Cl_8].nH_2O$

Compounds of this type were first obtained by the reduction of pertechnetate ions by metallic zinc in concentrated hydrochloric acid at approximately 100 °C.[5] Later this method was used with some modifications in other studies also for the preparation of salts of octachloroditechnetate ions.[17-22] The reduction of pertechnetate ions under the given conditions is as a rule accompanied by the formation of brown solutions, which are rapidly oxidised in air to greenish-blue solutions with $\lambda_{max} \cong 615$ nm,[5] which corresponds to the absorption of light by the $[Tc_2Cl_8]^{3-}$ ions. When salts with the cations $M^+ = K^+$, NH_4^+, $^1/_3Y^{3+}$, or

Table 1. The physicochemical properties of technetium cluster compounds.

No.	Compound [references to method of synthesis]	m, (n)	Magnetic properties: μ_{eff}, 300 K; μ_{eff}, 80 K; θ	Refs.	$\epsilon(Tc3d_{5/2})$, eV; $\epsilon(X)$, eV; References	Structural data: sp. gr.; (Z)	a, Å; b, Å; c, Å	α, deg; β, deg; γ, deg	$R(Tc_2-Tc)$, Å	$R(Tc-L_{eq})$, Å; $R(Tc-L_{ax})$, Å	Refs.
1	$K_3[Tc_2Cl_8O_2]$, [11, 13]	4.5; (2.0)	4.15; 3.69; −40	[13]	256.8; 268.9; [13.57]	—	—	—	—	—	—
2	TcO_2, [66]	4.0; (1.0)	1.5; 1.0; −200	[13]	255.2; —; [57]	—	5.53 (1); 4.79 (1); 5.53 (1)	90; 120; 90	~2.5	—	[66]
3	$[Tc_2(H_2EDTA)_2\mu\text{-}O_2]\cdot 5H_2O$, [65]	4.0; (~2.0)	D	[65]	—	$Pna2_1$; (4)	18.41 (1); 10.96 (1); 16.25 (1)	90; 90; 90	2.331 (1)	μ=O —1.913 (8); O—2.011 (7); N—2.207 (16)	[65]
4	$[(C_4H_9)_4N]_2[Tc_2Cl_8]$, [13, 22, 27, 51]	3.0; (4.0)	D	[13,22]	255.8; 268.5; [57]	$P2_1/c$; (4)	10.915 (3); 15.382 (3); 16.469 (2)	90; 122.37; 90	2.147 (4)	2.33 (1)	[27]
5	$[(C_4H_9)_4N]_2[Tc_2Br_8]$, [13, 22]	3.0; (4.0)	D	[13,22]	—	—	—	—	—	—	—
6	$Tc_2[(CH_3)_3CCOO]_4Cl_2$, [17]	3.0; (4.0)	D	[17]	—	$I4/m$; (2)	11.515 (2) 11.515 (2) 10.625 (3)	90; 90; 90	2.192 (1)	2.032 (4); 2.408 (4)	[17]
7	$Tc_2(Cl_3COO)_4Cl_2$, [49]	3.0; (4.0)	D	[49]	—	—	—	—	—	—	—
	$K_5(H_3O)[Tc_2Cl_8]_3\cdot 3H_2O$, [6]						12.80 (5); 12.80 (5); 8.30 (4)	90; 90; 120	2.144 (17)	2.38 (13) 3.53 (1)	[25,26]
8	$K_3[Tc_2Cl_8]\cdot 2H_2O$, [16]	2.5; (3.5)	1.74; 1.74; 0	[13,47]	255.5; 269.0; [57]	$P3_121$; (3)	12.838 (3); 12.838 (3); 8.197 (2)	90; 90; 120	2.117 (2)	2.364 (16); 3.579 (3)	[16]
	$K_6'K_{3-x}''(H_3O)_x[Tc_2Cl_8]\cdot nH_2O$ [a]						12.817 (3); 12.817 (3); 8.185 (2)	90; 90; 120	2.119 (1)	2.363 (14); 3.578 (1)	
9	$Cs_3[Tc_2Cl_8]\cdot 2H_2O$, [6]	2.5; (3.5)	2.17; —; —	[6]	—	$P3_121$; (3)	12.90 (5); 12.90 (5); 8.70 (4)	90; 90; 120	—	—	[25,26]
10	$(NH_4)_3[Tc_2Cl_8]\cdot 2H_2O$, [5, 6]	2.5; (3.5)	1.74; 1.74; 0	[13]	255.5; 269.0; [13.57]	$P3_121$ (3)	13.04 (2); 13.04 (2); 8.40 (1)	90; 90; 120	2.13 (1)	2.36 (3); —	[14,15]
11	$Y[Tc_2Cl_8]\cdot 2H_2O$, [5, 21]	2.5; (3.5)	~1.74; —; —	[21]	—	$P42_12$; (4)	11.712 (2) 11.712 (2) 7.661 (2)	90; 90; 90	2.105 (1)	2.363 (4); —	[21]
12	$(C_5H_5NH)_3\cdot[Tc_2Cl_8]\cdot 2H_2O$, [7]	2.5; (3.5)	~1.8; —	[7]	—	—	—	—	—	—	—
13	$(C_9H_7NH)_3[Tc_2Cl_8]\cdot 2H_2O$, [8]	2.5; (3.5)	2.08; 1.84; —	[8]	—	—	—	—	—	—	—
14	$[(C_4H_9)_4N]_3[Tc_2Cl_8]$, [13, 22]	2.5; (3.5)	1.73; 1.74; 0	[13]	—	—	—	—	—	—	—
15	$K_3[Tc_2Br_8]\cdot 2H_2O$, [13]	2.5; (3.5)	1.73; 1.73; 0	[13]	—	$P3_121$; (3)	13.63 (1); 13.63 (1); 8.46 (1)	90; 90; 120	—	—	[13]
16	$(NH_4)_3[Tc_2Br_8]\cdot 2H_2O$, [13]	2.5; (3.5)	1.73; 1.73; 0	[13]	—	—	—	—	—	—	—
17	$[Tc_2(C_5H_5N)_2Cl_5]$, [39]	2.5; (3.5)	1.8; —; —	[39]	255.3; 268.8; [57]	—	—	—	—	—	—
18	$[Tc_2(CH_3COO)_4Cl]$, [9]	2.5; (3.5)	1.73; 1.75; 0	[13,47]	255.8; 268.3; [57]	$C2/c$; (1)	15.035 (3); 7.801 (1); 12.894 (4)	90; 109.65; 90	2.117 (1)	2.065 (5); 2.656 (1)	[36]
19	$K[Tc_2(CH_3COO)_4Cl_2]$, [9]	2.5; (3.5)	1.73; 1.74; 0	[13,47]	255.8; 268.2; [57]	$P4_2/n$; (4)	11.9885 (3); 11.9885 (3); 11.4443 (2)	90; 90; 90	2.1260 (5)	2.07 (1); 2.589 (1)	[38]
20	$[Tc_2(o\text{-}C_5H_4ON)_4Cl]$, [18]	2.5; (3.5)	1.7; — —	[18]	—	$I4/m$; (2)	11.793 (3); 11.793 (3); 7.454 (1)	90; 90; 90	2.095 (1)	2.087 (3); 2.679 (1)	[18]
21	$[Tc_2(CH_3COO)_4Br]$, [10]	2.5; (3.5)	1.74; 1.74; 0	[13,47]	255.7; 181.4; [57]	$C2/m$; (1)	7.102 (3); 14.772 (4); 7.095 (2)	90; 113.36; 90	2.112 (1)	2.060 (4); 2.843 (1)	[37]

Table 1 (contd)

No.	Compound [references to method of synthesis]	m, (n)	Magnetic properties: μ_{eff}, 300 K; μ_{eff}, 80 K; θ	Refs.	$\varepsilon(Tc3d_{5/2})$, eV; $\varepsilon(X)$, eV References	Structural data: sp. gr.; (Z)	a, Å; b, Å; c, Å	α, deg; β, deg; γ, deg	R(Tc–Tc), Å	R(Tc–L_{eq}), Å; R(Tc–L_{ax}), Å	Refs.
22	$Tc_4O_5 \cdot nH_2O$, [13, 23]	2.5; (3.5)	1.75; 1.74; 0	[13]	255.9; —; [57]	—	—	—	—	—	—
23	$M_2[Tc_2Cl_6] \cdot nH_2O$, M=$NH_4$, K, [10, 13]	2.0; (5.0)	D	[10]	254.9; 268.9; [57]	—	—	—	—	—	—
24	$M_2[Tc_2Br_6] \cdot nH_2O$, M=$NH_4$, K, [10, 13]	2.0; (5.0)	D	[10]	254.6; 181.4; [57]	—	—	—	—	—	—
25	$[(R)_4N]_2[Tc_2X_6]$; R=C_2H_5, C_4H_9; X=Cl, Br, [13]	2.0; (5.0)	D	[13]	—	—	—	—	—	—	—
26	$[(CH_3)_4N]_3 \cdot [Tc_6Cl_6\mu\text{-}Cl_6]Cl_2$, [12, 13]	1.83; (4.0); (0.5)	~1.7; ~1.6; 0	[12,13]	254.6; 268.9; 270.5; [13]	$Pcmn$; (4)	11.583 (2); 13.527 (3); 24.387 (3)	80; 90; 90	2.16 (1) 2.69 (1)	2.38 (1); μ-Cl—2.38 (2); ~3.0	[79]
27	$[(CH_3)_4N]_2[Tc_6Cl_6\mu\text{-}Cl_6]$, [12]	1.67; (3.0); (1.0)	~1.1; ~0.8; —	[12]	—	$P\bar{1}$; (2)	11.614 (4); 11.633 (4); 14.017 (6)	69.66; 65.89; 60.13	2.22 (1); 2.57 (1)	2.40 (1); μ-Cl—2.45 (1); ~3.2	[76]
28	$[H_3O(H_2O)_3]_2 \cdot [Tc_6Br_6\mu\text{-}(Br, OH)_6]$ *, [10, 13]	1.67; (1.0)	~0.7; ~0.7; —	[13]	—	$P2_1/c$; (2)	9.258 (4); 9.211 (3); 17.437 (7)	90; 101.09; 90	2.59 (1)	2.55 (1); μ-Br—2.46 (2);	[79]
29	$[Tc_6Br_4\mu\text{-}Br_8]Br[H(H_2O)_2]$ *, [10, 13]	1.5; (4.0); (1.0); (0.5)	~1.0; ~0.6; —	[13]	254.7; 181.1; 182.8; [57]	$P2_1/n$; (2)	7.561 (2); 13.553 (5); 12.620 (3)	90; 102.62; 90	2.155 (3); 2.531 (2); 2.70 (2)	2.53 (2); μ-Br—2.51 (2); ~3.0	[78]
30	$[Tc_6Br_4\mu\text{-}Br_8]Br_2[H(H_2O)_2]_2$*, [12]	1.5; (4.0); (1.0); (0.5)	~1.1; ~0.7; —	[12]	—	$P2_1/a$; (2)	22.151 (9); 9.026 (3); 9.396 (4)	90; 105.94; 90	2.152 (9); 2.520 (9); 2.69 (1)	2.52 (1); μ-Br—2.52 (1); ~2.9	[76]
31	$[Tc_2(CO)_{10}]$, [67]	0; (1.0)	D	[67]	—	—	14.65 (1); 7.18 (1); 14.93 (1)	90; 105.6; 90	3.04 (1)	2.00 (1); 1.90 (1)	[67]
32	$[MTc(CO)_{10}]$, M=Mn, Re, [71]	0; (1.0)	D	[71]	—	—	—	—	—	—	—

Notation: $\varepsilon(X)$ is the energy of the electrons in the Cl_{2s} or $Br_{2p_{3/2}}$ skeleton, θ the Weiss constant, m the formal oxidation state of technetium, n the formal multiplicity of the Tc–Tc bonds, D a diamagnetic compound, and sp.gr. the space group.

*In these compounds there is a possibility that OH^- or H_3O^+ ions are present instead of H_2O molecules (or conversely).

**The results of a study by the authors of the review together with M.S.Grigor'ev and P.A.Koz'min.

$(C_4H_9)_4N^+$ are added to these solutions, crystals of complexes with the overall general formula $M_3[Tc_2Cl_8].nH_2O$ are formed[17–22] (Table 1).

Another method of synthesis of the octachloroditechnetate consists in the reduction of complexes of technetium(IV)–technetium(VII) in concentrated hydrochloric acid with molecular hydrogen under pressure in an autoclave at 120–180 °C.[6–8,11–13] As in the reduction with metallic zinc, the autoclave reduction is accompanied by the formation of brown solutions (λ_{max} = 465 nm), which are rapidly oxidised in air to greenish-blue solutions (λ_{max} = 645 nm). The reduction in autoclave proceeds at an initial hydrogen pressure of ~3 MPa. When technetium(IV) complexes are used as the initial compounds in the synthesis, the working temperature of the autoclave must be higher by 20–40 °C than in the case of pertechnetates, since the hexahalogenotechnetates(IV) are as a rule less soluble than the corresponding pertechnetates. Compounds having the composition $M_3[Tc_2Cl_8].nH_2O$, where $M^+ = K^+$, Cs^+, NH_4^+, PyH^+, or $QuinH^+$ are formed when salts with the cations $M^+ = K^+$, NH_4^+, $^1/_3Y^+$, or $(CuHg)_4N^+$ are added to these solutions[17–22] (Table 1).

All the octachloroditechnetates are substances which crystallise in the form of dark hexahedral needles, which give rise to a pale-grey powder on being ground. The complexes dissolve in hydrochloric acid with formation of turquoise solutions, which rapidly oxidise in air or disproportionate in its absence at low concentrations of the $[Tc_2Cl_8]^{3-}$ ions (~10^{-4} M) and are comparatively stable at high concentrations of such ions (~10^{-1} M). These compounds are sparingly soluble in polar organic solvents (clusters with organic cations are dissolved more effectively). In non-polar solvents the octachloroditechnetates do not dissolve, while in water and alkalies they rapidly hydrolyse with formation of brown colloidal solutions of the hydrated oxide $Tc_4O_5.nH_2O$.[23,24]

The autoclave method of synthesis of clusters with the $[Tc_2Cl_8]^{3-}$ anions[6-8] made it possible to observe an interesting phenomenon, which had not been noted by other workers[5,14-16,19-21] and which involves a non-stoichiometric variable content of certain singly-charged cations (M^+ = K^+, NH_4^+, or Cs^+) in octachloroditechnetate salts having the general formula $M_3[Tc_2Cl_8].nH_2O$. It was found that the composition of these clusters depends greatly on the hydrochloric acid concentration in the mother liquor from which they crystallise. For example, at an HCl concentration of 4–5 M, the K : Tc : Cl ratios in the potassium octachloroditechnetate formed are ~3 : 2 : 8, while in concentrated HCl solutions the ratios approach 2 : 2 : 8. A decrease of the content of K^+ ions in the complexes is accompanied by a decrease of the content of their water of crystallisation.

We may also note that the composition of these compounds depends on other factors as well, in particular on the rate of crystallisation. However, analysis of the diffractometer traces for the potassium octachloroditechnetate powders, obtained under different conditions, showed that the complex undergoes no appreciable crystal-chemical changes: the positions of all the lines on the diffractometer traces remain unchanged and correspond to the dimensions of the trigonal unit cell (a = 12.80 ± 0.05 Å; c = 8.30 ± 0.04 Å[25]), while the slight alteration of the intensities of the individual lines is mainly associated with the presence of a texture in the specimens.

One can assume *a priori* that the cause of the variable composition of the octachloroditechnetates may be either a variable oxidation state of technetium or the substitution of some of the cations by the H_3O^+ ions. The first version was proposed initially,[6] since the accuracy (±0.017 Å) of the X-ray diffraction study by a photomethod[25] precluded the determination of fine differences between the Tc–Tc distances in the $[Tc_2Cl_8]^{3-}$ and $[Tc_2Cl_8]^{2-}$ anions, which amount to ~0.03 Å according to the latest X-ray diffraction data[16,26,27] (Table 1). After revised X-ray diffraction data had been obtained,[16,21,26,27] an attempt was made to determine the H_3O^+ ions in potassium octachloroditechnetate, which led to their detection from the weak characteristic absorption lines in the infrared spectra [ν(OH) = 2965, 2930, and 2865 cm^{-1}; $\delta(OH)_2$ = 1610 cm^{-1} [28,29]]. The results did not conflict with the revised X-ray diffraction data,[26] according to which the K^+ ions in the unit cell of potassium octachloroditechnetate (+2.5) are present in two non-equivalent positions: sixfold (K′) and threefold (K″) (Fig.1); under these conditions, the sixfold positions were fully occupied by K^+ ions, while the threefold positions were half-occupied.

Summarising all that has been said above concerning the structure of the octachloroditechnetates(+2.5), one may conclude that their true composition is described by a formula with variable coefficients, namely $M'_6M''_{3-x}(H_3O)_x.[Tc_2Cl_8]_3.nH_2O$, where x and n vary from 0 to 3. The

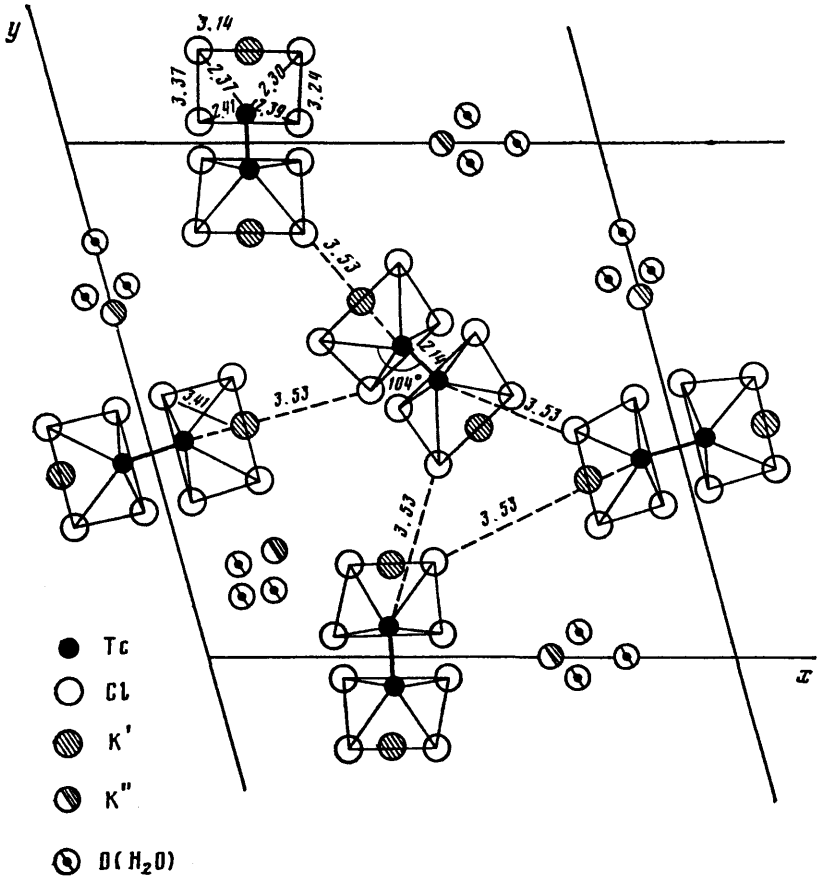

Figure 1. Projection of the unit cell of $K_6(H_3O)[Tc_2Cl_8]_3.3H_2O$ onto the xy plane.[25,26]

substitution of some of the M^+ ions by H_3O^+ ions is possible by virtue of the similarity of the properties of the hydronium cation and the alkali metal cations both in solutions and in the crystalline state.[30,31] The knowledge of such fine differences between the compositions of the octachlorodi-technetates(+2.5) is useful mainly for the study of certain solid-phase reactions, since the dissolution of these compounds leads to their dissociation into the M^+, H_3O^+, and $[Tc_2Cl_8]^{3-}$ ions and the properties of the solutions are then determined by the concentration of the octachloroditechnetate ions. The simplified formula of these complexes $M^3[Tc_2Cl_8].nH_2O$ was therefore used in subsequent studies.[7-13]

The structure of the ammonium,[14,15] potassium,[16,25,26] and yttrium[21] salts of the anion $[Tc_2Cl_8]^{3-}$ (Figs.1 and 2; Table 1) has been investigated by X-ray diffraction. The characteristic features of the molecular structure of this anion are its eclipsed conformation (D_{4h} symmetry) and a short Tc–Tc distance, much shorter than the analogous distance in metallic technetium (~2.70 Å[1]). It is striking that the change of the cation leads to an alteration of the Tc–Tc distance by ~0.04 Å (Table 1). We may note that the influence of the nature of the cation on the metal–metal distance in the rhenium and molybdenum complexes of the type $[M_2X_8]^{n-}$ (where M = Re or Mo and X = Cl or Br) with a quadruple M–M bond is weaker (the distance changes by ~0.02 Å[4,32-34]). In the case of technetium the true change in the M–M bond length on replacing the cations in the octachloroditechnetates is apparently somewhat smaller than the unduly high experimental value owing to the low accuracy of the X-ray diffraction study.[25,26]

(b) The Octabromoditechnetates $M_3[Tc_2Br_8].nH_2O$

When the potassium and ammonium halide complexes of technetium(VII)–technetium(IV) are reduced with molecular hydrogen under pressure (~3 MPa) in an autoclave in concentrated hydrobromic acid at 120–140 °C, the corresponding octabromoditechnetates(+2.5) of the type $M_3[Tc_2Br_8].2H_2O$ (where M = NH_4 or K), which are isostructural with the analogous cluster technetium chlorides,[12,13] are formed. Since the $[Tc_2Br_8]^{3-}$ ions are much less stable than $[Tc_2Cl_8]^{3-}$,[10-13,24] the formation of the octabromoditechnetates is observed only in a mixture with technetium(II) and technetium(IV) bromide complexes. This mixture can be conveniently resolved under the microscope using the distinctive characteristics of the octabromoditechnetates(+2.5) (large hexahedral needles or conglomerates of the latter, whose comminution yields a pale-brown powder). The octabromoditechnetates(+2.5) are sparingly soluble in polar and non-polar organic solvents, hydrolyse rapidly in water and alkalies, and dissolve in concentrated hydrogen halide acid solutions with formation of the $[Tc_2Br_8]^{3-}$ ions, which rapidly oxidise to $[TcBr_6]^{2-}$ or, in the absence of oxidants, disproportionate to $[Tc_2Br_6]^{2-}$ and $[TcBr_6]^{2-}$.[13,24]

(c) Dinuclear Cluster Compounds with a Structure of the "Lantern" Type

$Tc_2(o\text{-}C_5H_4ON)_4Cl$. Green crystals of $[Tc_2(o\text{-}C_5H_4ON)_4]Cl$, with sublime *in vacuo* (~10^{-9} Pa) at 350 °C without decomposition, have been obtained by the reaction of ammonium octachloroditechnetate with *o*-hydroxypyridine in nitrogen at 150 °C.[18] The compound is sparingly soluble in organic and inorganic solvents. Fig.3 illustrates the molecular structure of this cluster, which has the D_{2h} symmetry.

In contrast to $[Tc_2Cl_8]^{3-}$, the Tc–Tc bond in the oxopyridine cluster is additionally strengthened by four $o\text{-}C_5H_4ON$ bridging ligands, which have a contracting effect and lead to structures of the "lantern" type. The shortening of the Tc–Tc bond in the oxopyridine dinuclear cluster relative to the octachloroditechnetates(+2.5) amounts to ~0.015 and is close to the analogous value for dinuclear rhenium(III) clusters.[35]

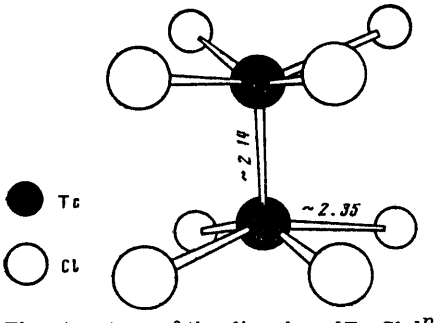

Figure 2. The structure of the dinuclear $[Tc_2Cl_8]^{n-}$ (n = 2 or 3) ions (according to a number of investigations[14,15,21,25-27]).

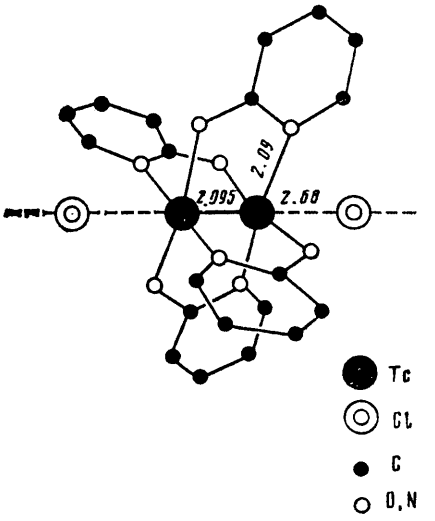

Figure 3. Fragment of the $[Tc_2(o\text{-}C_5H_4NO)_4Cl]$ structure.[18]

Acetate complexes. When $K_3[Tc_2X_8].2H_2O$ or $K_2[Tc_2X_6].2H_2O$ (where X = Cl or Br) interacts with glacial acetic acid in an autoclave at 120–200 °C in an argon or molecular hydrogen atmosphere (3–5 MPa), green crystals of the acetate dinuclear complexes having a structure of the "lantern" type are formed: $K[Tc_2(CH_3COO)_4]Cl_2$ and $[Tc_2(CH_3COO)_4]X$ (where X = Cl or Br)[9-11] (Table 1, Figs.4–6). The compounds are readily soluble in polar organic solvents and water and give rise to pale-green solutions, which gradually darken in air. On dissolution in concentrated hydrogen halide acid solutions, the corresponding octahalogenoditechnetates(+2.5) are formed.

Technetium acetate complexes without inorganic cations are volatile at ~400 °C like the oxopyridine complex which has a similar structure.

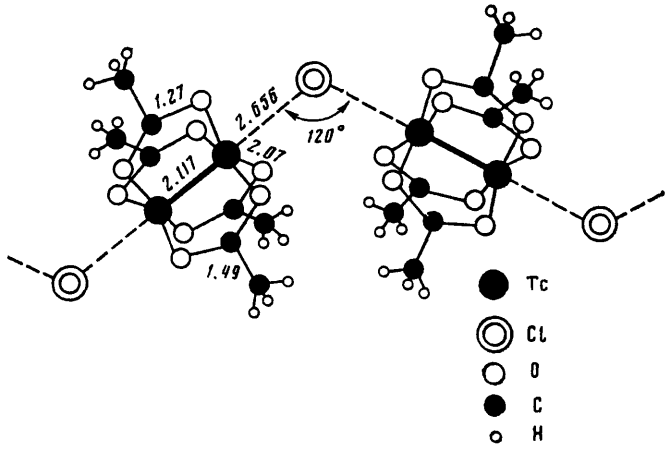

Figure 4. Fragment of the $[Tc_2(CH_3COO)_4Cl]$ structure.[36]

(d) Compounds Which Have Not Been Investigated by X-ray Diffraction

$Tc_4O_5.nH_2O$. A black powder, whose composition can be expressed by the overall formula $Tc_4O_5.14H_2O$, has been obtained by the hydrolysis of $K_3[Tc_2Cl_8].2H_2O$ in argon.[13] The freshly prepared hydrated oxide dissolves in concentrated hydrochloric acid with formation of $[Tc_2Cl_8]^{3-}$ ions. This demonstrates the retention of M–M bonds of high multiplicity in the hydrated oxide. The structure of $Tc_4O_5.14H_2O$ or its thermal degradation are accompanied, according to ESCA, infrared spectroscopic, and X-ray diffraction data[13] by irreversible structural changes. The final dehydration product is the black oxide Tc_4O_5.

The X-ray electronic and infrared spectra of Tc_4O_5 indicate the non-equivalence of technetium atoms as well as the oxygen atoms in its structure but this is not associated with the formation of a metallic technetium phase, TcO_2, or other known technetium oxides on dehydration of $Tc_4O_5.14H_2O$. According to magnetic measurements (Table 1), on the hydrated and anhydrous oxides, there is approximately one unpaired electron for each two technetium atoms, as in all the dinuclear d^4–d^5 clusters. The exact structure of the two compounds is unknown, but the set of chemical and physicochemical properties suggests the presence of Tc–Tc bonds with a high multiplicity in their structure.

$[Tc_2(C_5H_5N)_2Cl_5]$. The thermal decomposition of pyridinium octachloroditechnetate(+2.5) in argon at 250–280 °C yielded the compound $[Tc_2(C_5H_5N)_2Cl_5]$, the chemical analysis of which as well as optical and X-ray electronic spectra (Table 1) made it possible to ascribe to it a dinuclear structure with a Tc–Tc bond having a high multiplicity and with pyridine and chloride ligands.[39] The molecular structure of the compound is so far unknown. It has been isolated in the form of a dark-brown powder soluble in pyridine and unstable on dissolution in inorganic acids and alkalies. Treatment with nitric acid or a peroxide–alkali mixture as well as prolonged storage in air lead to its oxidation to technetium(IV) in the form of the stable compound $[Tc(C_5H_5N)_2Cl_4]$. In water the complex $[Tc_2(C_5H_5N)_2Cl_5]$ rapidly hydrolyses, while in alkalies it dissolves with decomposition.

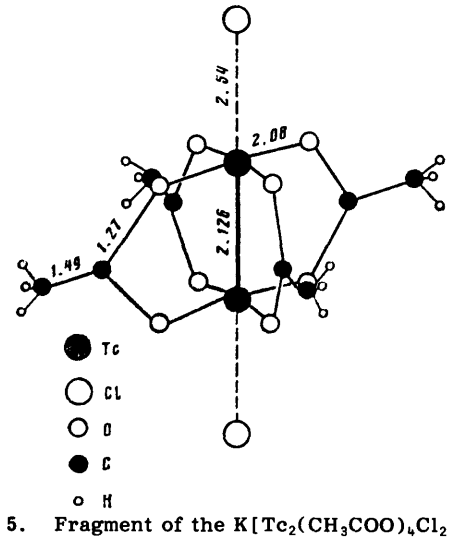

Figure 5. Fragment of the $K[Tc_2(CH_3COO)_4Cl_2]$ structure.[38]

(e) The Electronic Structure of Dinuclear d^4–d^5 Clusters

The d^4–d^5 clusters are of considerable experimental and theoretical interest, because they constitute so far the only representatives of dinuclear clusters of *d* transition elements with multiple M–M bonds having this electronic structure†. Attempts have been frequently made to examine the electronic structure of these compounds. According to the MO scheme for the quadruple M–M bond in dinuclear clusters with D_{4h} symmetry (Fig.7), the "superfluous" ninth electron in $[Tc_2Cl_8]^{3-}$ in isoelectronic clusters can be in one of the following MO: $b_{1u}(\delta^*_{M-M})$;[19,20,40,41] $a_{2u}(\sigma'_{n,\,M-M})$;[14,15,42,43] $a_{1g}(\sigma''_{M-M})$.[44] There exist indirect data confirming each of these versions but none of the confirmations constitute direct and well founded experimental results.

The claim by Cotton and co-workers[19,20,40] that the unpaired electron in the $[Tc_2Cl_8]^{3-}$ anion is in the $b_{1u}(\delta^*_{M-M})$ orbital has received somewhat more justification than others. This conclusion was reached on the basis of quantum-chemical calculations,[40] optical spectroscopic experiments,[1] and EPR of frozen solutions.[20] However, the accuracy of the quantum-mechanical calculations of the highest MO is not high and more reliable results, which are in no way directly dependent on these calculations, are provided in this instance by the EPR method. However, the EPR spectra

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†The synthesis and electronic structure of the dinuclear d^4–d^5 rhenium cluster $\{Re_2Cl_4[P(n\text{-}C_3H_7)_3]_4\}PF_6$ have been described,[45,46] but its molecular structure has not so far been confirmed by X-ray diffraction.

(and hence also their interpretation) quoted by Cotton and Pedersen[20] arouse certain doubts. Indeed, Cotton and Pedersen[20] recorded the EPR spectra of frozen solutions of $Y[Tc_2Cl_8].9H_2O$ in a mixture of 10 vol.% of concentrated hydrochloric acid and 90 vol.% of ethanol and later it became known[13,23] that the $[Tc_2Cl_8]^{3-}$ ions undergo solvolytic reactions in such a mixture. This affects the charge of the dinuclear anions and their optical spectra, so that the EPR spectra obtained under these conditions refer to a mixture of species of the type $[Tc_2Cl_{8-n}.(Solv)_n]^{(3-n)-}$. As a result of this, the resolution of the $[Tc_2Cl_8]^{3-}$ spectrum is low, particularly that of parallel orientation lines, which might have been the cause of the inaccuracy in the determination of the parameters of the EPR spectra.

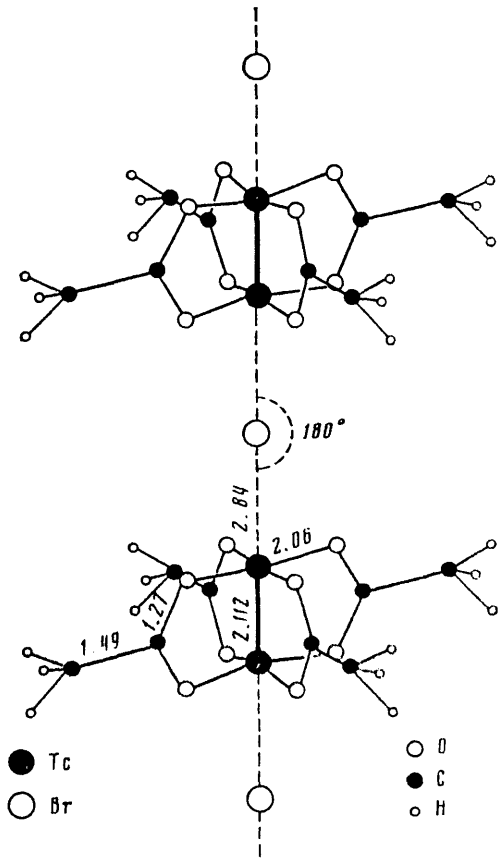


Figure 6. Fragment of the $[Tc_2(CH_3COO)_4Br]$ structure.[37]

A combined magnetochemical study of a whole series of paramagnetic dinuclear technetium clusters with a d^4–d^5 configuration of the central atoms has been carried out recently.[13,47,48] It was shown that a single broad signal with an effective g-factor of 2.09 ± 0.02 is observed in the EPR spectra of polycrystalline clusters. Their effective magnetic moment μ_{eff} does not vary with temperature and corresponds to a spin-only value for a single unpaired electron per molecule (~1.74 μ_B).

The differences between μ_{eff} and the spin-only value observed previously in other studies and their temperature dependence (Table 1) have been attributed either to the inaccuracy of the magnetochemical experiments for low amounts of the technetium compounds or to the presence of an admixture of high-spin technetium(IV) complexes.

The EPR spectra[13,47,48] of frozen vitreous specimens of the Tc_2^{5+} complexes are similar in form and give rise to a well-resolved hyperfine structure due to the two equivalent ^{99}Tc nuclei with a nuclear spin of 9/2. It has also been established that the parameters of the EPR spectra of all the technetium clusters investigated (Table 1, compounds 8, 10, 15, 16, 18, 19, and 21) agree to within experimental error and have the following values: $g_\parallel = 1.85 \pm 0.03$; $g_\perp = 2.13 \pm 0.03$; $A_\parallel = -(188 \pm 5) \times 10^{-4}$ cm^{-1}; $A_\perp = -(78 \pm 5) \times 10^{-4}$ cm^{-1}; $P = (5 \pm 1) \times 10^{-4}$ cm^{-1}. The absence of a dependence of the magnetochemical parameters of the solutions and polycrystalline substances on temperature and the nature of the ligands surrounding the Tc_2^{5+} fragment as well as the observation that $g_\parallel < 2$, $g_\perp > 2$, and $g_{av} > 2$ can be accounted for by the fact that the unpaired electron in this dinuclear fragment is in the $b_{1u}(\delta^*_{M-M})$ MO formed in the main from the $4d_{xy}$ atomic orbitals (AO) of the two equivalent technetium atoms (Table 2). In other words, the formal multiplicity of the M–M bond in the d^4–d^5 complexes is 3.5. Thus the experimental results confirm the main conclusions reached earlier from calculations of the electronic structure of $[Tc_2Cl_8]^{3-}$ by the X_α method.[40]

Table 2. The possible ground electronic states and the ratios of the g-factors in the Tc_2^{5+} cluster compounds.[13,47,48]

Ground state	HOMO	Technetium AO forming the HOMO	n	Energy of interacting MO	g_{theor}		
					$g_\parallel$	$g_\perp$	g_{av}
B_{1u}	δ^*_{M-M}	$4d_{xy}$	3.5	$E(b_{2u}) > E(b_{1u}) > E(e_u)$	<2	>2	≳2
A_{1g}	σ'_{M-M}	$5s+4d_{z^2}+5p_z$	4.5—4.0	$E(e_g) > E(a_{1g})$	~2	≲2	~2
B_{2g}	δ'_{M-M}	$4d_{xy}$	4.5	$E(e_g) > E(b_{1g}) > E(b_{2g})$	<2	<2	<2
A_{2u}	σ''_{M-M}	$5s+4d_{z^2}+5p_z$	4.5—4.0	$E(a_{2u}) > E(e_u)$	~2	>2	≳2
B_{1g}	δ''_{M-M}	$4d_{x^2-y^2}$	4.5	$E(e_g) > E(b_{1g}) > E(b_{2g})$	>2	<2	~2
E_g	π^*_{M-M}	$4d_{xz}+4d_{yz}$	3.5	$E(b_{1g}) > E(e_g) > E(b_{2g})$	—	—	—

2. Dinuclear Cluster Compounds of Technetium with the d^4–d^4 Electronic Configuration of the Central Atoms

Compounds 4–7 (Table 1) belong to this group. The physicochemical properties of the given dinuclear clusters are close to those of the analogous rhenium and molybdenum compounds with the quadruple M–M bonds and are as a rule isostructural with them.[4,32–34]

(a) Dinuclear Cluster Compounds with a Structure of the "Lantern" Type

$\{Tc_2[(CH_3)_3CCOO]_4\}Cl_2$. The first dinuclear d^4–d^4 technetium complex was obtained by Cotton and Gage[17] and an attempt was made to substitute the chloride ions in the coordination sphere of $[Tc_2Cl_8]^{3-}$ by trimethylacetate ions. The substitution reaction was carried out by heating (t = 150 °C) a suspension of $(NH_4)_3[Tc_2Cl_8].2H_2O$ in pivalic acid under argon for 36 h. After the reaction mixture had been

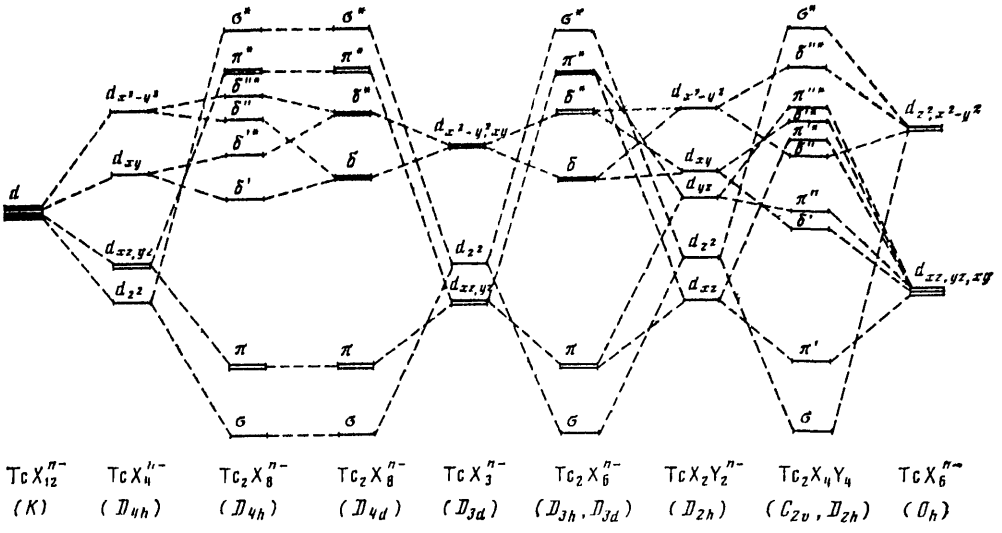


Figure 7. A simplified schematic illustration of the formation of one-electron metallic MO in dinuclear clusters of different symmetry.

cooled, fine red crystals of $\{Tc_2[(CH_3)_3CCOO]_4\}Cl_2$ precipitated; one of them was subjected to X-ray diffraction (Fig.8, Table 1), which demonstrated the similarity of the crystalline and molecular structures with dinuclear technetium and rhenium pivalate complexes.

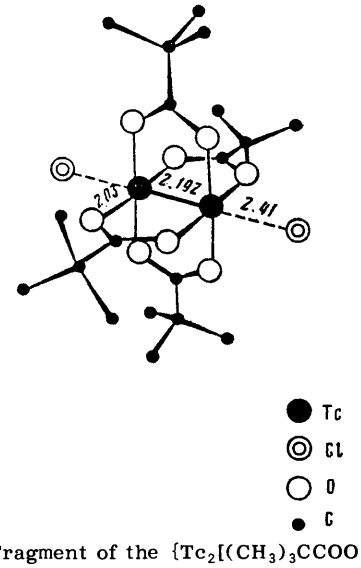


Figure 8. Fragment of the $\{Tc_2[(CH_3)_3CCOO]_4\}Cl_2$ structure.[17]

$[Tc_2(CH_3COO)_4]Cl_2$. The reduction of $[TcO_4]^-$ in a mixture of acetic and hydrochloric acids by molecular hydrogen under pressure yielded red crystals of $[Tc_2(CH_3COO)_4]Cl_2$.[49] The structure of the compound was not investigated by X-ray diffraction, but, in view of the fact that the technetium and rhenium[50] acetate complexes are isostructural, presumably it too has a structure of the "lantern" type with four bridging acetate ions in the equitorial planes and two axial chlorine atoms on either side of the quadruple Tc–Tc bond, i.e. their structure is similar to that of $\{Tc_2[(CH_3)_3CCOO]_4\}Cl_2$ (Fig.8). This structure of the acetate complex has also been confirmed by its diamagnetism and infrared spectroscopic data.

(b) The Octahalogenoditechnetates $M_2[Tc_2X_8]$

$[(C_4H_9)_4N]_2(Tc_2Cl_8)$. In contrast to $[Mo_2Cl_8]^{4-}$ and $[Re_2Cl_8]^{2-}$, the octachloroditechnetate ions have been obtained and characterised by means of chemical,[51] spectroscopic,[22] and X-ray diffraction[27] analytical methods comparatively recently. This is due to the lower stability of the $[Tc_2Cl_8]^{2-}$ ion compared with $[Tc_2Cl_8]^{3-}$ in hydrochloric acid solutions in which dinuclear cluster chlorides are as a rule formed on reduction of technetium(VII)–technetium(IV) by various reductants. However, subsequent investigations showed that the $[Tc_2Cl_8]^{2-}$ ions are much more stable in organic solvents than $[Tc_2Cl_8]^{3-}$.

This property of the octachloroditechnetate ions has been used to develop an optimum method for the synthesis of compounds with the $[Tc_2Cl_8]^{2-}$ anion.[13] For this purpose, the oxo-, oxochloro-, or chloro-complexes of technetium(VII)–technetium(IV) were reduced in concentrated hydrochloric acid (H_3PO_2, metallic zinc, or molecular hydrogen under a pressure of 3–5 MPa in an autoclave at ~140 °C can be used as reductants). An excess of a hydrochloric acid solution of tetrabutylammonium chloride is added to the resulting solution of the mixture of $[Tc_2Cl_8]^{2-}$, $[Tc_2Cl_8]^{3-}$, and $[Tc_2Cl_6]^{2-}$ ions and the solution is then extracted with a mixture of chloroform, carbon tetrachloride, and methylene chloride a characteristic feature of which is a satisfactory separation of the organic and aqueous phases. In order to

increase the solubility of technetium ions in the organic phase, acetone may also be added to the extraction mixture. When the solution is coloured an intense brown or turquoise, which corresponds to the presence of a high content of $[Tc_2Cl_6]^{2-}$ or $[Tc_2Cl_8]^{3-}$ ions respectively in the mixture, it is necessary to pass air through the extraction mixture until it becomes fully coloured bright green, but a yellow colour, indicating the formation of the $[TcCl_6]^{2-}$ ions, is not obtained. After this, the organic phase is separated and allowed to stand in air in order to evaporate the solvent slowly. Crystallisation yields bright green $[(C_4H_9)_4N]_2[Tc_2Cl_8]$ dendrites, which are less soluble than $[(C_4H_9)_4N]_2[TcCl_6]$. After two recrystallisations from acetone or methylene chloride, a pure preparation of tetrabutylammonium octachloroditechnetate is produced. Following the repeated employment of the evaporated mother liquors, formed in all the stages of the experiment, as the starting materials for the reduction of technetium chloride complexes to technetium(III), the overall yield of tetrabuytylammonium octachloroditechnetate can be increased almost to ~100%.

The preparation of crystals of tetrabutylammonium octachloroditechnetate has been described by Cotton et al;[27] they were studied by X-ray diffraction, which showed that the structure of the $[Tc_2Cl_8]^{2-}$ ions is analogous to that of the isoelectronic cluster rhenium and molybdenum chlorides and bromides with a quadruple M–M bond[4,32–36] (Fig.2 and Table 1).

Table 1 shows that the replacement of the chloride ions in $[Tc_2Cl_8]^{2-}$ by trimethylacetate ions $[(CH_3)_3CCOO]^-$ leads to an appreciable increase of the Tc–Tc distance, which is caused by the *trans*-influence of the axial chlorine atoms in $\{Tc_2[(CH_3)_3CCOO]_4\}Cl_2$ on the length of the quadruple M–M bond. The mechanism of the *trans*-influence consists in the fact that the formation of the $Tc-Cl_{ax}$ bond in the carboxylate complexes involves mainly the $4d_{z^2}$, $5s$, and $5p_z$ electrons of the technetium atoms and the $3p_z$ electrons of the chlorine atoms. Since the $4d_{z^2}$, $5s$, and $5p_z$ electrons of technetium also participate in the formation of the σ-component of the Tc–Tc bond (Fig.7), there is a mutual correlation of the $Tc-Cl_{ax}$ and Tc–Tc bond lengths. Analogous effects have been observed for the dinuclear complexes of rhenium, molybdenum, chromium, platinum metals, etc.[4,32–34,52,53]

$[(C_4H_9)_4N]_2[Tc_2Br_8]$. When several drops of hydrobromic acid are added to an acetone solution of $[(C_4H_9)_4N]_2[Tc_2Cl_8]$ and the reaction mixture is then heated briefly to boiling, a carmine-red solution is formed; this colour corresponds to the $[Tc_2Br_8]^{2-}$ ions.[22] When the solution is evaporated, carmine-red $[(C_4H_9)_4N]_2[Tc_2Br_8]$ dendrites are formed, but their exact molecular structure has not so far been established.

(c) The Electronic Structure of Dinuclear d^4–d^4 Clusters

All the dinuclear technetium complexes with the d^4–d^4 electronic configuration of the central atoms known at present are diamagnetic. According to the one-configuration approximation, the eclipsed conformation of these complexes, like that of the isoelectronic Cr, Mo, W, and Re compounds having no bridging ligands, is determined by the δ-component of the M–M bond formed mainly as a result of the overlap of the $4d_{xy}$ AO of the M atoms.[4,32–34,41,42] Fig.7 illustrates a simplified scheme for the formation of the M–M bond in dinuclear clusters with the D_{4h} symmetry, from which it follows that the highest MO in the d^4–d^4 complexes is the $b_{2g}(\delta_{M-M})$ orbital, while the M–M bond has a formal multiplicity of 4.0.

After the determination of the formal multiplicity of the Tc–Tc bonds in $[Tc_2Cl_8]^{n-}$ (n = 2, 3) and its isoelectonic technetium complexes, the question arises of the cause of the lower stability of the dinuclear d^4–d^4 clusters compared with the d^4–d^5 clusters and of the possibility of the formation of analogous dinuclear complexes by other d elements with a multiplicity of the M–M bonds of 3.5. It has been shown[13,41,48,54] that the real electronic structure of the clusters of d transition elements can be described within the framework of the MO method only when account is taken of configuration interactions (CI). Thus allowance for the CI in the d^4–d^4 complexes results in a decrease of the effective multiplicity of the M–M bond approximately to 3.0; on the other hand, allowance for the CI in the d^4–d^5 complexes hardly affects the effective multiplicity of the M–M bond, which is a direct consequence of the Brillouin theorem,[55] according to which singly excited states do not contribute to the ground electronic state of the system when account is taken of the CI by the self-consistent field methods. The quadruple bond in the d^4–d^4 complexes is therefore "diluted" as a result of the doubly excited $\sigma^2\pi^2\delta^0(\delta^*)^2$ state with an M–M double bond, whereas in the d^4–d^5 complexes the low-lying excited $\sigma^2\pi^2\delta^0(\delta^*)^1$ state makes no contribution to the overall M–M bond energy, while all the doubly excited states, occupying high positions, make a very small contribution to the ground state.

The above mechanism of the increase of the stability of the clusters with a single unpaired electron does not extend to all the dinuclear clusters of the d transition elements. It is known that the d^4–d^3 molybdenum clusters, namely $[Mo_2Cl_8]^{3-}$ and $[Mo_2(SO_4)_4]^{3-}$, are much less stable than their analogues with a quadruple M–M bond, i.e. $[Mo_2Cl_8]^{4-}$ and $[Mo_2(SO_4)_4]^{4-}$.[4,32–34] An analogous phenomenon has been observed for the dinuclear rhenium complexes $[Re_2X_8]^{3-}$, which have not so far been isolated in a pure form and whose formation has been observed only in electrochemical processes.[20,56] The complex $\{Re_2Cl_4[P(n\text{-}C_3H_7)_3]_4\}PF_6$[45,46] (where the Re–Re bond length is so far unknown) apparently constitutes an exception to this rule; the increase of its stability may be caused by the σ-donor influence of the phosphine ligands, which increases the energy of the σ-component of the Re–Re bond compared with the $[Re_2Cl_8]^{2-}$ and $[Re_2Cl_6(PR_3)_2]$ complexes.

Allowance for the CI should not therefore always increase the stability of the dinuclear clusters with a single unpaired electron. We believe than an additional cause[13] is the decrease of the effective charge Z_{eff} on the metal atoms following the formation of an M–M bond by the latter. This phenomenon had been recently observed for technetium clusters by X-ray electronic spectroscopy.[57,58] An analogous decrease of Z_{eff} is not observed in the rhenium clusters, while in the molybdenum clusters [judging from the skeletal electron energies $\varepsilon(Re_{4f_{7/2}})$ and $\varepsilon(Mo_{3d_{5/2}})$],[59–64] Z_{eff} is actually increased on the metal atoms following the formation of M–M bonds.

Estimates of the influence of the addition (or removal) of the "superfluous" electron to certain rhenium, technetium, and molybdenum clusters with the d^4–d^4 configuration have been published.[13] They showed that in the case of technetium clusters the addition of the "superfluous" electron does indeed result in the maximum gain in the repulsion energy between M atoms with like charges, the gain being greater than the loss in the δ-overlap energy. Conversely, the removal of a single electron always leads to an increase of the repulsion energy with a simultaneous decrease of the δ-overlap energy. From this it follows that the d^4–d^3 complexes should be always less stable in relation to the dissociation of the M–M bonds than the d^4–d^4 complexes with a

similar structure. We may note that the factor involving the increase of the ionic radius with decrease of the oxidation state of the metal atoms in the cluster acts in the opposite direction. Whether or not the acceptance of a superfluous electron in the d^4–d^4 system has a favourable effect depends on the ratios of all these factors. In the case of technetium the addition of the electron is energetically favourable not only for dinuclear clusters but, as will be shown below, also for the polynuclear clusters.

Cotton et al[21] recently gave another explanation of the strengthening of the M–M bonds in the d^4–d^5 technetium clusters compared with the d^4–d^4 clusters. The explanation is based on the hypothesis that, on passing from $[Tc_2Cl_8]^{2-}$ to $[Tc_2Cl_8]^{3-}$, the decrease of the energy of the δ-component of the M–M bond is accompanied by the simultaneous increase of the energy of the π- and possibly also the σ-component of this bond. If this hypothesis is valid, then, on passing from the d^4–d^4 complexes to the d^4–d^5 complexes, either an increase of the energy difference between the π_{M-M} and π^*_{M-M} MO, on the one hand, and the σ_{M-M} and σ^*_{M-M} MO, on the other, or an increase of the "metallic" character of the π_{M-M} and σ_{M-M} MO should take place.

However, the X-ray electronic spectroscopic data[13,57] have shown that none of these conditions is in reality fulfilled. For example, an increase of the splitting between the lines corresponding to the π- and δ-components of the M–M bond in the valence X-ray electronic spectrum is not observed on passing from the $[Tc_2Cl_8]^{2-}$ ion to $[Tc_2Cl_8]^{3-}$ and $Tc_2(CH_3COO)_4X$ (where X = Cl or Br) (the lines of the σ-components of the Tc–Tc bond are not shown in the spectra). An increase of the "metallic" character of the σ_{M-M} and π_{M-M} MO would have been manifested by a decrease of $\varepsilon(Tc_{3d_{5/2}})$ on passing from the d^4–d^4 complexes to the d^4–d^5 complexes, since this would have entailed an appreciable decrease of Z_{eff} on the technetium atoms. However, the real decrease of $\varepsilon(Tc_{3d_{5/2}})$ is small and corresponds to an average decrease of this quantity with decrease of the formal oxidation states of technetium by 0.5. Furthermore, with increase of the energy of the σ-component of the M–M bond in the d^4–d^4 complexes, the energy of the skeletal electrons of the axial halogen atoms would have decreased appreciably; however, the real values of $\varepsilon(Cl_{2p_{3/2}})$ and $\varepsilon(Br_{3d_{5/2}})$ (Table 1) correspond to typical values of this electron energy in the dinuclear clusters of other *d* elements.[52,53,59,60]

3. Dinuclear Clusters of Technetium Compounds with the d^5–d^5 Electronic Configuration of the Central Atoms

Six complexes with this electronic structure, having the general formula $M_2[Tc_2X_6].nH_2O$, where M = K, NH_4, or $(C_4H_9)_4N$, X = Cl or Br, and *n* = 0 or 2, have been described hitherto[10,12,13] (Table 1, compounds 23–25). These compounds are formed under the conditions of far-reaching reduction of the technetium halide complexes in concentrated solutions of the corresponding hydrogen halides. The $[Tc_2X_8]^{3-}$ ions are the direct precursors of $[Tc_2X_6]^{2-}$. Atomic hydrogen (metallic zinc or aluminium in concentrated HCl) or molecular hydrogen (under a 3–5 MPa pressure in an autoclave at 140–180 °C) can be used as the reductant. The compounds are dark-brown cryptocrystalline powders or conglomerates of acicular crystals forming flat and three-dimensional stars. The complexes are sparingly soluble in organic polar and non-polar solvents, the $[(C_4H_9)_4N]_2[Tc_2X_6]$ salts constituting an exception, since they are easily soluble in polar organic solvents and readily dissolve in hot solutions of the corresponding hydrogen halides with formation of brown solutions, which are rapidly oxidised in air to $[Tc_2X_8]^{3-}$ and further to $[TcX_6]^{2-}$. All compounds of this type are diamagnetic. The X-ray electronic spectra[13,57] (Table 1) indicate the absence of bridging halogen atoms from the molecules of these compounds.

There are at present no X-ray diffraction data for the structures of the $M_2[Tc_2X_6].nH_2O$ complexes, but the set of their chemical and physicochemical properties indicates their dinuclear structure with an M–M bond having a high multiplicity. The D_{3h} or D_{3d} symmetry of the $[Tc_2X_6]^{2-}$ ions is the most likely. Evidently, for this symmetry of the dinuclear complexes, the $4d_{xy}$ and $4d_{x^2-y^2}$ AO of technetium becomes degenerate (Fig. 7) and the Tc–Tc bond in the $[Tc_2X_6]^{2-}$ ions is quintuple—of the $\sigma^2\pi^2\delta^2_{xy}\delta^2_{x^2-y^2}$ type in contrast to the hypothetical dinuclear d^5–d^5 complexes with D_{4h} symmetry in which the multiplicity of the M–M bond would have been three: $\sigma^2 2\pi^2\delta^2_{xy}(\delta^*_{xy})^2$.

We may note that in this case the rotation of one of the (TcX_3) fragments about the Tc–Tc bond by 60° does not result in a gain of the δ-overlap energy; the hindered conformation with D_{3d} symmetry (the ethane-like structure), in which the interligand repulsions are manifested to the smallest extent, should therefore be the most preferred for the $[Tc_2X_6]^{2-}$ ions.[13]

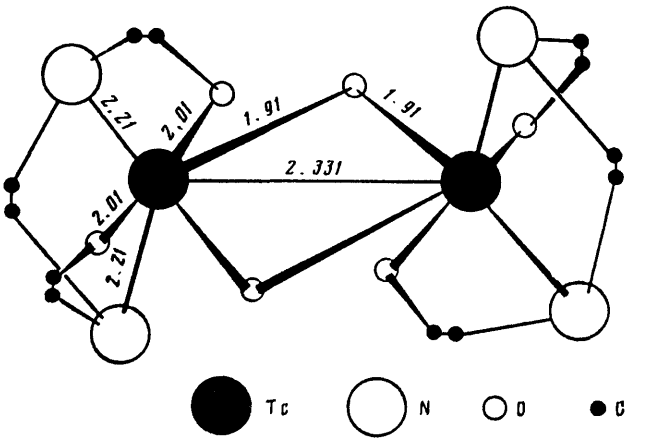


Figure 9. Schematic illustration of the immediate environment of the technetium atoms in the $[Tc_2(H_2EDTA)_2\mu\text{-}O_2].5H_2O$ structure (according to the data of Burgi et al[65]).

4. Dinuclear Clusters of Technetium Compounds with the d^3–d^3 and d^3–d^2 Electronic Configurations of the Central Atoms

$[Tc_2(\mu\text{-}O)_2(H_2EDTA)_2].5H_2O$. This compound has been obtained by reducing $[TcO_4]^-$ with an excess of $NaHSO_3$ in the presence of an excess of Na_2H_2EDTA with heating (70–80 °C) of the reaction mixture for several days.[65] After recrystallisation from 0.01 M $HClO_4$, the complex consisted of a diamagnetic cryptocrystalline red-brown powder. In constrast to all the dinuclear technetium clusters examined above, the ethylenediamine tetra-acetate complex with two bridging oxygen atoms, additionally binding the technetium

atoms, has the idealised C_{2v} symmetry. The ethylenediaminetetra-acetate ions behave as tetradentate ligands, coordinating each technetium atom to 2 nitrogen atoms and 2 oxygen atoms in the acetate group (Fig.9); the coordination polyhedra of the technetium atoms formed in this process consist of two distorted octahedra with a common edge made up of bridging oxygen atoms.

TcO_2. Technetium dioxide has a structure close to that of the ethylenediaminetetra-acetate complex described above#. According to the results of X-ray diffraction analysis of the TcO_2 powder,[66] the technetium dioxide cluster has a distorted rutile structure: six oxygen atoms are located at the vertices of a distorted octahedron in the centre of which the technetium atom is present (Fig.10). The TcO_6 octahedra are linked to one another along the edges made up of oxygen atoms forming an infinite three-dimensional network. The technetium atoms in the octahedra have been brought closer together in pairs so that one may expect the formation of Tc–Tc bonds, but their strength is much lower (and their length much greater—see Table 1) than in the ethylenediaminetetra-acetate complex. This is shown indirectly by the paramagnetism of technetium dioxide, indicating the presence of approximately one unpaired electron at each technetium atom.[13]

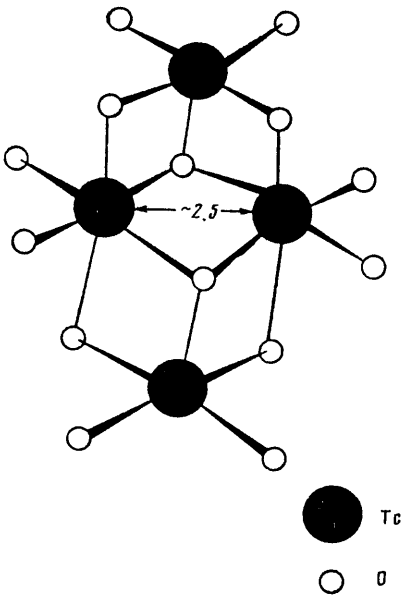


Figure 10. Fragment of the TcO_2 structure (according to the data of Magneli and Andersson[66]).

$K_3[Tc_2Cl_8O_2]$. This compound is hitherto the only representative of dinuclear technetium clusters with the d^3–d^2 electronic configuration of the central atoms. The complex has been obtained by refluxing a solution of $K_3[Tc_2Cl_8].2H_2O$ in ethyl methyl ketone in air.[11,13] This compound is a yellow–green powder sparingly soluble in ethyl methyl ketone and other organic solvents and readily soluble in inorganic acids. The complex is resistant to the action of oxidants and reductants both in the solid phase and in solutions. It can be oxidised to $[TcO_4]^-$ only after prolonged refluxing with strong oxidants such as Ce^{4+} in 0.4 M H_2SO_4. In the presence of complex-forming agents (for example, concentrated hydrochloric acid), the $[Tc_2Cl_8O_2]^{3-}$ ions decompose comparatively rapidly with formation of initially equivalent amounts of $[TcCl_6]^{2-}$ and $[TcOCl_5]^{2-}$.

Infrared spectroscopy of $K_3[Tc_2Cl_8O_2]$ indicates the presence of two types of bonds between the oxygen and technetium atoms in the structure of this complex: $\nu(Tc{=}O) = 1020\ cm^{-1}$ (strong); $\nu(Tc{-}O) = 680\ cm^{-1}$ (medium); $\delta(Tc{-}O{-}Tc) = 475\ cm^{-1}$ (medium). The X-ray electronic spectra of this compound[57] indicate the absence of bridging chlorine atoms from its structure. Thus, although there are no direct data concerning the structure of $K_3[Tc_2Cl_8O_2]$, the physicochemical properties of this complex suggest that it has a dinuclear structure with a weak metal–metal bond.

The electronic structure of the hypothetical complex $[(NH_3)_2(OH)_2Tc(\mu\text{-}O)_2Tc(OH)_2(NH_3)_2]$, with a molecular structure analogous to that of the complex $[Tc_2(\mu\text{-}O)_2(H_2EDTA)_2]$, has been calculated[65] by the extended Hückel method. The calculation led to the conclusion that a single Tc–Tc bond with the $\sigma^2\pi^2(\delta^*)^2$ electronic structure is formed in the technetium ethylenediaminetetra-acetate complex and not a triple bond ($\sigma^2\pi^2\delta^2$), which might have been suggested on the basis of the scheme in Fig.7. According to Burgi et al,[65] the reverse sequence in terms of the energy of the δ_{M-M} and δ^*_{M-M} MO responsible for the formation of the δ(Tc–Tc) bond in the given complex arises by virtue to the destabilising effect of the 2*p* orbitals of the bridging oxygen atoms. This explains the greater length of the Tc–Tc bond in the ethylenediaminetetra-acetate complex (~2.33 Å) compared with the expected length of the "truly" triple M–M bond.

However, even if this type of effect, involving the destabilisation of the δ(Tc–Tc) bond under the influence of bridging ligands, does occur, its extent is not as great as has been suggested.[65] Indeed, Table 1 shows that the expected length of the Tc–Tc triple bond should be ~2.22 Å, i.e. shorter by ~0.1 Å than in the ethylenediaminetetra-acetate complex. On the other hand, the length of the single Tc–Tc bond should be ~2.55 Å, which is greater by ~0.23 Å than the analogous length in $[Tc_2(\mu\text{-}O)_2(H_2EDTA)_2].5H_2O$. From this it follows that the difference between the energies of the δ_{M-M} and δ^*_{M-M} MO should be positive (and not negative as suggested by Burgei et al[65]) and greater in absolute magnitude than the energy of the interelectron repulsion, since otherwise the complex $[Tc_2(\mu\text{-}O)_2(H_2EDTA)_2].5H_2O$ would have been paramagnetic with two unpaired electrons (as in the case of TcO_2).

Thus it is most likely that the formal multiplicity of the Tc–Tc bond in the ethylenediaminetetra-acetate complex is 3.0 ($\sigma^2\pi^2\delta^2$). However, the δ-component of the bond is weakened, so much that its contribution to the overall energy of the M–M bond is close to zero.

The δ-level is apparently destabilised to an even greater extent in the TcO_2 and $[Tc_2Cl_8O_2]^{3-}$ complexes having a similar structure, which leads to their paramagnetism (Table 1), the value of μ corresponding to the presence of two or three unpaired electrons per molecule.

The methods of synthesis and properties of TcO_2 have been described in detail in a monograph.[1]

5. The Cluster Carbonyls

Several technetium carbonyl complexes in which metal–metal bonds are observed have been described.

$[Tc_2(CO)_{10}]$. Ditechnetium decacarbonyl was first obtained simultaneously by two groups of investigators[67,68] via the reaction

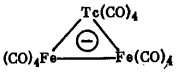
$$Tc_2O_7 + 17CO \rightarrow [Tc_2(CO)_{10}] + 7CO_2 .$$

The carbonylation was carried out in an autoclave at ~200 °C and an initial carbon monoxide pressure of ~20 MPa. It was later reported[69] that the carbonylation of TcO_2 with formation of ditechnetium decacarbonyl also takes place under milder conditions: ~2 MPa and 250 °C.

The compound $[Tc_2(CO)_{10}]$ is a colourless crystalline substance with a melting point of ~160 °C, which readily sublimes *in vacuo* (~10^{-4} Pa) at 50 °C. The compound is diamagnetic and readily dissolves in diethyl ether and other non-polar organic solvents.

In contrast to the molecules of the dinuclear complexes discussed above, the $[Tc_2(CO)_{10}]$ molecule (Fig.11 and Table 1) has the following structural features: (1) idealised D_{4d} symmetry (staggered conformation); (2) a weak M–M bond; (3) a higher strength of the bonds between the technetium atoms and axial ligands than that of the bonds involving equatorial ligands. In broad outline, the structure of the ditechnetium decacarbonyl molecule resembles those of $[Mn_2(CO)_{10}]$ and $[Re_2(CO)_{10}]$.[70] The chemical and physicochemical properties of these compounds are likewise similar. For example, the interaction of $[M_2(CO)_{10}]$ (where M = Mn, Tc, or Re) with elemental halogens in organic solvents results in the formation of compounds of the type $M(CO)_5X$ (where X = Cl, Br, or I), i.e. the oxidative addition of the X_2 molecules to the M–M bond, accompanied by dissociation, takes place.[69] The interaction of $M(CO)_5X$ with dimetal decacarbonyls in the presence of sodium amalgam results in the formation of mixed carbonyls of the type $[MnTc(CO)_{10}]$ and $[ReTc(CO)_{10}]$,[71] whose structure resembles that of ditechnetium decacarbonyl.

Irradiation of a mixture of ditechnetium decacarbonyl and iron pentacarbonyl (in molar proportions of 1 : 4) with ultraviolet light in tetrahydrofuran for 1 h yielded the mixed technetium iron carbonyl cluster $[Fe_2Tc(CO)_{12}]^-$.[72] The anion was also precipitated in the form of the tetrabutylammonium salt. A trinuclear structure of this anion has been postulated:[70]



The formation of an M–M bond is also possible in the dimeric technetium carbonyl halides having the general formula $[Tc(CO)_4X]_2$ (where X = Cl, Br, or I), which are formed when $[Tc_2(CO)_{10}]$ interacts with elemental halogens in carbon tetrachloride or chloroform on heating in a sealed tube.[69]

The interaction of cobalt carbonyl in tetrahydrofuran in the presence of an excess of the Na/K alloy in an atmosphere of CO at room temperature for 1 h yielded the anion $[Co(CO)_4]^-$, which reacted with $[Tc(CO)_5X]$ to form after 5 h a yellow-red compound having the composition $[CoTc(CO)_9]$, which is readily soluble in organic solvents. The diamagnetism of this complex suggests the presence of the heteropolar M–M bond in its structure.[73]

The formation of M–M bonds may also be expected in the structure of the polynuclear technetium tetracarbonyl hydride having the tentative structure $[HTc(CO)_4]_3$.[74]

The compound is formed as the side product in the synthesis of $[HTc(CO)_5]$ [69,75] by the interaction of ditechnetium decacarbonyl with sodium amalgam in tetrahydrofuran with subsequent acidification of the reaction mixture using concentrated orthophosphoric acid.

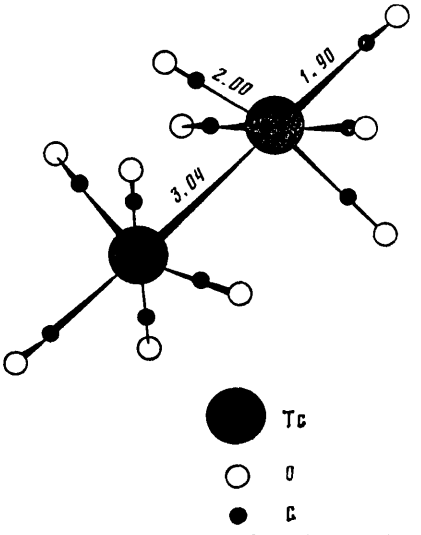


Figure 11. Molecular structure of $Tc_2(CO)_{10}$ (according to the data of Hileman et al[67]).

It is seen from the data for the chemistry of cluster technetium carbonyls presented above that in the case of strong-field ligands technetium exhibits a tendency towards the formation of clusters. In terms of this property, technetium resembles the platinum group elements.

6. Polynuclear Cluster Compounds of Technetium

Until recently, there was no information in the literature about polynuclear ($n > 4$) clusters not only of technetium but also of all the Group VIIB elements. However, such compounds are known[2,3] for Group V, VI, and VIII transition metals and the elements of the vanadium and chromium subgroup clusters with weak-field ligands have been observed, while for the platinum subgroup metals clusters with strong-field ligands have been found. Thus the possibility of the formation of polynuclear clusters by Group VIIB elements and, in particular, of technetium clusters with weak-field ligands is of undoubted interest for general chemistry.

The first communications about the synthesis[10,13] and structure[76–79] of polynuclear technetium halides appeared in 1982–83. These studies demonstrated the enhanced capacity of technetium for the formation of polynuclear clusters with metal–metal bonds. Furthermore, the compounds isolated constituted a type of cluster compounds with conjugated quadruple metal–metal bonds previously unknown for other elements. It was therefore useful to consider in greater detail the results of studies in the chemistry of polynuclear technetium clusters carried out at the present time by the authors of this review.

In the deliberate search for ways to form polynuclear technetium clusters, the authors were guided by the following postulates:[13] (1) the stability and probability of the formation of polynuclear clusters should be greater in the case of a smaller effective charge on the technetium atoms, i.e. for complexes with a lower electronegativity of the ligand; (2) it is most likely that the polynuclear technetium clusters constitute a kind of intermediate link in the reduction of dinuclear clusters with multiple Tc–Tc bonds to the metallic state; (3) other conditions being equal, the probability of the formation of polynuclear clusters should be greater at high concentrations of technetium ions in solutions; (4) in the presence of a large assortment of reductants capable of reducing dinuclear technetium clusters to polynuclear clusters, it is preferable to employ reductants which do not contaminate the final products.

It was found[10,13] that all the requirements enumerated above are satisfied by the autoclave method for the reduction of technetic acid in concentrated hydrogen halide solutions by molecular hydrogen under a pressure of 3–5 MPa at 140–220 °C. A series of experiments showed that the final product of the reduction of $H(TcO_4)$ under these conditions is a mixture of outwardly similar crystalline substances with similar physicochemical properties. The mixture composition can be described by the general overall formula $[TcX_{1.8\pm0.3}\cdot .m(H_2O, OH^-, H_3O^+)]_n$, where X = I or Br and $n > 2$§.

According to X-ray electronic data,[13,57] the technetium atoms in the compounds comprising this mixture are in an average oxidation state of 2.0–1.5 [a single narrow peak with $\varepsilon(Tc_{3d_{5/2}}) = 254.7 \pm 0.3$ eV for X = Br and $\varepsilon(Tc_{3d_{5/2}}) = 254.5 \pm 0.3$ eV for X = I is observed in the spectra], while the halogen atoms in the structures of these compounds belong to at least two types: terminal [$\varepsilon(Br_{3p_{3/2}}) = 181.1 \pm 0.3$ eV; $\varepsilon(I_{4d_{5/2}}) = 48.4 \pm 0.4$ eV] and bridging [$\varepsilon(Br_{3p_{3/2}}) = 182.8 \pm 0.3$ eV; $\varepsilon(I_{4d_{5/2}}) = 49.8 \pm 0.4$ eV]. Magnetic data indicate a weak paramagnetism of the $[TcX_2.0.5H_2O]_n$ complexes, which include ~1 unpaired electron for 4–6 technetium atoms¶.

The results of the studies of the physicochemical properties of $[TcX_2.0.5H_2O]_n$ described above suggested a polynuclear structure of the compound constituting this mixture. Subsequently this hypothesis was confirmed by the X-ray diffraction analysis of single crystals of a series of compounds forming part of a mixture of polynuclear technetium bromides.[13,76–79] Using the differences between the outer appearances and physicochemical properties of the crystals, initially investigated by methods of microcrystal chemical analysis, it was later possible to achieve an initial resolution of the mixture into its constituent parts under the microscope. Such resolution made it possible subsequently to investigate thoroughly the physicochemical properties of each phase in $[TcBr_2.0.5H_2O]_n$ and to develop the optimum methods for the synthesis of these compounds. Methods for the synthesis of hexanuclear tetramethylammonium chloride cluster compounds of technetium were developed analogously.

(a) Polynuclear Cluster Bromides

$[Tc_8Br_4\mu\text{-}Br_8]Br[H(H_2O)_2]$. This octanuclear technetium cluster is the first representative of polynuclear clusters of *d* transition elements with a complex system of M–M bonds including four conjugated quadruple Tc–Tc bonds. The compound is formed on reduction of a concentrated solution of $H[TcO_4]$ or $H_2[TcBr_6]$ by molecular hydrogen under pressure (3–5 MPa) in an autoclave at 140–160 °C in concentrated hydrobromic acid. The complex crystallises in the form of black elongated tetrahedral prisms with a metallic cluster (a black powder is obtained on grinding). The crystals are insoluble in organic acids and polar and nonpolar organic solvents.

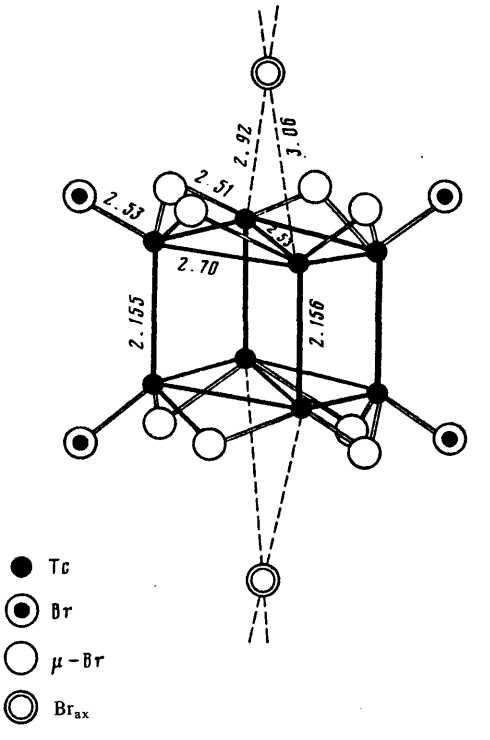


Figure 12. Fragment of the $[Tc_8Br_4\mu\text{-}Br_8]Br[H(H_2O)_2]$ structure.[78]

Fig.12 illustrates a fragment of the $[Tc_8Br_4\mu\text{-}Br_8]Br[H(H_2O)_2]$ structure. The molecule is constructed from four dinuclear Tc_2^{n+} fragments with quadruple M–M bonds located in vertical planes. Each of the eight technetium atoms is additionally bound in two "horizontal" planes by a system of M–M bonds forming two rhombs (upper and lower). Each

§ For brevity and also in view of the difficulty of the determination of the exact composition of this mixture, the above formula was used initially[10,13,57] and will be used in the present review in the form $[TcX_2.0.5H_2O]_n$.

¶ The values of μ_{eff} for $[TcX_2.0.5H_2O]$ have been determined with a low accuracy because the diamagnetic and paramagnetic contributions to the total magnetic susceptibility are comparable and the exact diamagnetic corrections for technetium compounds of this kind are unknown. For this reason, it was initially assumed[10] that the constituent compounds of this mixture are diamagnetic and only subsequent more accurate magnetic susceptibility data confirmed their weak paramagnetism,[13] the nature of which has not so been established.

technetium atom is also linked to two bridging bromine atoms which additionally span the technetium atoms in pairs in the horizontal planes. The technetium atoms located on the long diagonals of the rhombs form bonds also with the terminal bromine atoms; the remaining four technetium atoms are bound in pairs by weak electrostatic interactions in the vertical plane with two bromine atoms, each of which is analogously linked to a neighbouring polynuclear fragment.

The authors of the structural investigation[76–78] assume that the $[H(H_2O)_2]^+$ cations are present in the structure of the octanuclear complex instead of water molecules, although the location of hydrogen atoms was not established objectively. We believe[12,13] that this hypothesis requires additional investigation because the infrared spectra of this compound [namely the presence in the spectra of only the $\nu(O-H)_{H_2O} \cong 3500\ cm^{-1}$ and $\delta(H-OH)_{H_2O} \cong 1600\ cm^{-1}$ absorption bands] and its weak paramagnetism failed to confirm the presence of the $[H(H_2O)_2]^+$ cations.

$[Tc_8Br_4\mu\text{-}Br_8]Br_2[H(H_2O)_2]_2$. Under analogous conditions but at lower temperatures (130–150 °C) one of the products of the reduction of the $[TcO_4]^-$ or $[TcBr_6]^{2-}$ ions in hydrobromic acid is the complex $[Tc_8Br_4\mu\text{-}Br_8]Br_2[H(H_2O)_2]_2$. It crystallises in the form of black (without metallic lustre) elongated hexahedral prisms. On grinding, the crystals give rise to a black powder with a green tint which is soluble in hydrobromic acid and polar organic solvents with formation of a dark-green solution having a brown tint. The compound does not dissolve in non-polar organic solvents. According to preliminary data, this octanuclear complex is paramagnetic. However, a definite conclusion concerning the number of unpaired electrons is not so far possible owing to the difficulty of separating the phases and the low accuracy of the magnetochemical measurements for systems of this kind.

Preliminary X-ray diffraction data obtained for the $[Tc_8Br_4\mu\text{-}Br_8]Br_2[H(H_2O)_2]_2$ single crystal (the compound was synthesised by the authors of this review at the Institute of Physical Chemistry of the USSR Academy of Sciences and the X-ray diffraction analysis was carried out by P.A.Koz'min and co-workers at the Institute of General and Inorganic Chemistry of the USSR Academy of Sciences) have shown that its structure resembles that of $[Tc_8Br_4\mu\text{-}Br_8]Br[H(H_2O)_2]$ (Fig.12). The principal difference consists in the fact that in the case of $[Tc_8Br_4\mu\text{-}Br_8]Br_2[H(H_2O)_2]_2$ the octanuclear fragments made up of technetium atoms are not linked into infinite chains by weak electrostatic interactions with the axial bromine atoms and are separated from one another to give isolated molecules, while the axial bromine atoms are no longer bridging. The principal interatomic distances and angles in the structure of this complex are the same as in $[Tc_8Br_4\mu\text{-}Br_8]Br[H(H_2O)_2]$ (Table 1).

$[Tc_6Br_6\mu_3\text{-}(Br, OH)_6][H_3O(H_2O)_3]_2$. Following an increase of the synthesis temperature in the autoclave to ~180–200 °C and a slight decrease of the concentration of technetium ions in solution, one of the products of the reduction of $H[TcO_4]$ or $H_2[TcBr_6]$ in hydrobromic acid is a hexanuclear complex which has the tentative composition $[Tc_6Br_6\mu_3\text{-}(Br, OH)_6][H_3O(H_2O)_3]_2$ according to X-ray diffraction data for the single crystals.[79] The compound crystallises in the form of dark red-brown crystals (a red-brown powder is obtained after grinding), which are very readily soluble in polar organic solvents but less so in non-polar solvents and concentrated hydrobromic acid. The $[Tc_6Br_6\mu_3\text{-}(Br, OH)_6]^{2-}$ solutions are dark-brown and are stable in air. The hexanuclear complex is weakly paramagnetic (Table 1).[12,13]

The structure of the hexanuclear cluster technetium bromide[79] is similar to the structures of the known octahedral cluster molybdenum and tungsten halides.[2] The difference consists in the fact that in the case of technetium the positions of the bridging halogen atoms are not fully occupied (Fig.13) and some of these atoms have been substituted by bridging oxygen atoms, probably the oxygen atoms in the OH groups.

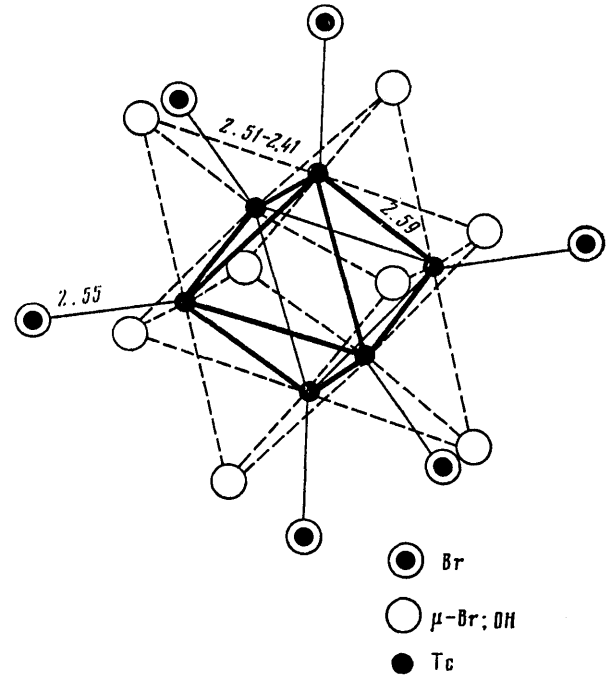


Figure 13. Fragment of the $[H_3O(H_2O)_3]_2(Tc_6Br_6\mu_3\text{-}(Br, OH)_6]$ structure (according to the data of Koz'min et al[79]).

Since X-ray diffraction analysis did not permit in this instance an unambiguous demonstration of the presence of hydrogen atoms in the structure, the above formula of the octahedral hexanuclear technetium complex cannot be regarded as finally established. Nevertheless, even the available data concerning the structure of the octahedral technetium cluster permit the important conclusion that, apart from the outer AO of the type $4d_{z^2}$, $4d_{xy,yz}$, and $4d_{x^2-y^2}$, also AO of the $4d_{xy}$ type are involved in the formation of its 15 bonding "metallic" MO.[13] We may note that a similar phenomenon has not been observed in the octahedral molybdenum and tungsten clusters, whose electronic structure is described by twelve bonding "metallic" MO formed by the AO of the metals of the d_{z^2}, $d_{xy,yz}$, and $d_{x^2-y^2}$ types.[2,80,81] Furthermore, one can state with confidence that in the technetium cluster 1–3 electrons are located in MO which are antibonding either in relation to

M–X† or M–M bonds. By virtue of the presence of these electrons, the cluster becomes paramagnetic and probably loses some of the bridging bromine atoms.

(b) Polynuclear Cluster Chlorides

The reduction of $[(CH_3)_4N]_2[TcCl_6]$ or $[(CH_3)_4N][TcO_4]$ in concentrated hydrochloric acid by molecular hydrogen under pressure (3–8 MPa) in an autoclave at 140–220 °C leads to the formation of a mixture of dark-brown almost black crystals of different geometrical shapes (tetrahedral rods, dendrides, and planar layer polyhedra). Using methods analogous to those described for $(TcBr_2.0.5H_2O)_n$, it was possible to resolve this mixture and to find the optimum conditions for the synthesis of crystals of two compounds: $[(CH_3)_4N]_3[Tc_6Cl_6\mu\text{-}Cl_6]Cl_2$ and $[(CH_3)_4N]_2[Tc_6Cl_6\mu\text{-}Cl_6]$#.

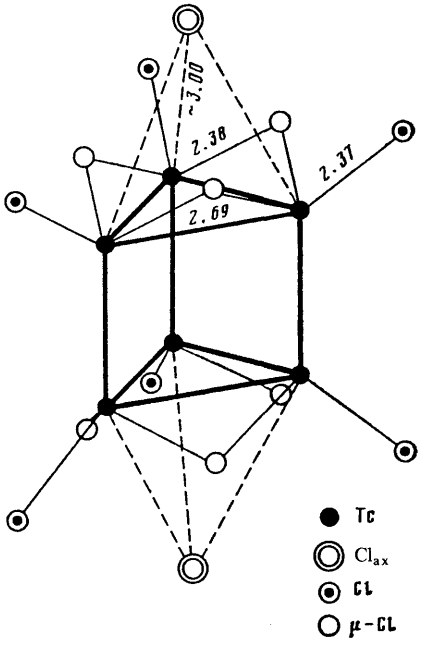


Figure 14. Fragment of the $[(CH_3)_4N]_3[Tc_6Cl_6\mu\text{-}Cl_6]Cl_2$ structure (according to the data of Koz'min et al[79]).

$[(CH_3)_4N]_3[Tc_6Cl_6\mu\text{-}Cl_6]Cl_2$ is formed with a maximum yield at 140–150 °C and an initial hydrogen pressure in the autoclave of 3–5 MPa. The compound forms elongated tetragonal rods—frequently conglomerates of such rods in the form of dendrites. After grinding, the crystals give rise to a dark-brown powder soluble in hydrochloric acid, water, alcohol, and other polar solvents, giving rise to brown solutions.[12,13]

The molecular structure of the compound is presented in Fig.14 and Table 1.[79] Evidently, in broad outline, the $\{[Tc_6Cl_6\mu\text{-}Cl_6]Cl_2\}^{3-}$ structure resembles that of the octanuclear cluster technetium bromide, but in the structure of the hexanuclear complex the Tc atoms are located at the vertices of a prism whose base consists of an equilateral triangle and not a rhomb as, for example, in the $[Tc_8Br_4\mu\text{-}Br_8].Br[H(H_2O)_2]$ structure. The vertical edges of this prism are much shorter than the horizontal edges and correspond to the quadruple Tc–Tc bonds, while the horizontal edges correspond to M–M bonds with a lower multiplicity. In addition, the technetium atoms are linked in the horizontal planes by bridging chlorine atoms. Furthermore, in the $[(CH_3)_4N]_3[Tc_6Cl_{12}]Cl_2$ molecule there are six terminal chlorine atoms and two chlorine atoms of the ionic type, which constitute a kind of axial ligands. The compound is paramagnetic (Table 1), μ_{eff} corresponding to the presence of approximately one unpaired electron per molecule.

$[(CH_3)_4N]_2[Tc_6Cl_6\mu\text{-}Cl_6]$ is formed under analogous but more severe conditions (150–180 °C) in an autoclave on reduction of $[(CH_3)_4N]_2[TcCl_6]$ or $[(CH_3)_4N][TcO_4]$ in concentrated hydrochloric acid. The crystals of this compound resemble anthracite under the microscope and have the form of orthorhombic layered plates. After grinding, a dark-brown powder with a violet tint is produced. It is soluble in hydrochloric acid, water, alcohol, and other polar solvents, giving rise to brown solutions. The complex is paramagnetic (Table 1) but it is so far impossible to specify with confidence the number of unpaired electrons in the molecule in view of the low accuracy of the magnetochemical study.

According to preliminary X-ray diffraction data, obtained by P.A.Kos'min and co-workers, the structure of the cluster is close to that of $[(CH_3)_4N]_3[Tc_6Cl_6\mu\text{-}Cl_6]Cl_2$ (Fig.14, Table 1). The differences consist in the length of the Tc–Tc bonds. For example, in the case of $[(CH_3)_4N]_2[Tc_6Cl_{12}]$ the three Tc–Tc bonds located in the vertical planes are lengthened at the expense of the shortening of the M–M bonds in two horizontal planes. Furthermore, the terminal chlorine atoms in the neighbouring polynuclear fragments play the role of axial ligands in the structure of this hexanuclear complex.

The similarity of the molecular structures of the hexanuclear technetium chlorides and the octanuclear technetium bromides suggests also the similarity of their electronic structures. For example, the vertical edges of the prism made up of the technetium atoms in the $[Tc_8Br_{12}]$, $[Tc_8Br_{12}]^+$, and $[Tc_6Cl_{12}]^-$ complexes (Figs.12 and 14 and Table 1) correspond to the quadruple M–M bonds {triple in the case of $[Tc_6Cl_{12}]^{2-}$}, formed, as in the dinuclear clusters, by the $4d_{z^2}$, $4d_{xz}$, $4d_{yz}$ AO of technetium. In addition, the $4d_{xy}$ and $4d_{x^2-y^2}$ AO of technetium also participate in the formation of this bond. However, the AO of the last two types are also involved in the formation of many-centre "metallic" MO in the horizontal planes.

Precisely because of the formation of these many-centre MO, the electron densities at the technetium atoms in the polyhedral cluster bromide are equalised, as shown by the equality of the values of $\varepsilon(Tc_{3d_{5/2}})$ for the formally heterovalent technetium atoms in these complexes (Table 1). The nature of these MO is such that they can have simultaneously both bonding (or antibonding) character in relation to

†This follows from the fact that the involvement of 5*s* AO of technetium in the formation of M–M bonds is unlikely, since they are as a rule[2–4] occupied in the formation of M–X bonds and the filling of the antibonding "metallic" MO by 7–9 electrons would have led to a considerable lengthening of the Tc–Tc bonds.

#K.E.German participated in the development of the method of synthesis of these compounds.

vertical M–M bonds and the bonding (or antibonding) character in relation to the Tc–Tc bonds in the horizontal planes. In other words, the many-centre "metallic" MO, formed mainly by the $4d_{xy}$ and $4d_{x^2-y^2}$ AO of technetium, are highly delocalised, while the remaining components of the M–M bonds remain predominantly localised at the pairs of technetium atoms.[13]

The sequence in the distribution of the many-centre MO in each specific instance can be different and depends, for example, on the ligand environment or the nuclearity of the cluster. The addition of new electrons to these MO therefore either does {as in the case of $[Tc_6Cl_{12}]^-$ and $[Tc_6Cl_{12}]^{2-}$} or does not {as in the case of $[Tc_8Br_{12}]^+$ and $[Tc_8Br_{12}]$} lead to a significant rearrangement of the system of M–M bonds in the cluster. On further addition of electrons to these MO, the role of the $4d_{xz}$, $4d_{yz}$, and even $4d_{z^2}$ AO of technetium in the formation of the many-centre M–M bonds is enhanced to an increasing extent, while their role in the formation of the Tc–Tc bonds located in the vertical planes is diminished. Ultimately, this leads to a radical rearrangement of the polynuclear cluster accompanied by the equalisation of the energies and lengths of all the M–M bonds—for example the octahedral $[Tc_6Br_6\mu_3\text{-}(Br, OH)_6]^{2-}$ cluster is formed.[13]

In conclusion of this Section, we may note that only the first steps have been taken in the chemistry of polynuclear cluster compounds of technetium: in the first place much remains obscure not only in the description of the electronic structure and mechanism of the formation of these compounds but also even in the determination of their exact composition. The unusual structure of these compounds, which have no analogues among the polynuclear clusters of other elements, the similarity of the properties and compositions of various compounds of this class to one another, and also the ease of their interconversions are all factors hindering the identification and isolation of the polynuclear technetium clusters in a pure state and hence also the investigation of their physicochemical properties. However, the data already available in this field indicate, on the one hand, the enhanced capacity of technetium for the formation of polynuclear clusters with weak-field ligands and, on the other hand, the "anomaly" in the properties of the technetium clusters compared with the typical clusters of other *d* elements. The increased capacity of technetium for the formation of paramagnetic clusters as well as clusters with a complex system of non-equivalent M–M bonds may be included among such "anomalous" properties.

III. CHEMICAL PROPERTIES IN SOLUTIONS

1. The Formation of M–M Bonds

A study[7] of the reduction of $[PyH]_2[TcCl_6]$ by molecular hydrogen under pressure in an autoclave in hydrochloric acid with a gradual increase of the working temperature showed that the $(PyH)_2.[Tc_2Cl_8]_3.2H_2O$ cluster is formed at an HCl concentration of 4–5 M. The $[TcCl_6]^{2-}$ ions, which are present prior to the formation of the clusters, are hydrolysed partially under these conditions at ~120 °C:

$$[TcCl_6]^{2-}+2H_2O\rightarrow[Tc(OH)_2Cl_4]^{2-}+2HCl. \qquad (1)$$

The hydrolysed technetium(IV) ions are readily reduced by molecular hydrogen, which is accompanied by the formation of M–M bonds:

$$[Tc(OH)_2Cl_4]^{2-} \xrightarrow{H_2} [Tc_2Cl_{8-x}(OH)_x]^{3-} \xrightarrow{HCl} [Tc_2Cl_8]^{3-}. \qquad (2)$$

The hydrolysed $[Tc_2Cl_{8-x}(OH)_x]^{3-}$ ions thus formed are rapidly converted into $[Tc_2Cl_8]^{3-}$ on interaction with concentrated hydrochloric acid. We may note that the substitution of chloride ions by H_2O molecules is also possible in reactions (1) and (2).

The above study[7] showed that the formation of $[Tc_2Cl_8]^{3-}$ ions must be preceded by a stage involving the formation of the hydrolysed clusters. The hydrolysis in an autoclave at an elevated temperature is promoted by a decrease of the concentration of hydrochloric acid as a result of its partial evaporation. We may note that the formation of hydrolysed cluster complexes is observed also in the reduction of technetium(IV) in concentrated hydrochloric acid on refluxing with metallic zinc.[5]

2. The Behaviour of the $[Tc_2X_8]^{3-}$ Ions in Solutions of Hydrogen Halides

In order to elucidate the causes of the increased stability of the hydrolysed cluster ions compared with the unhydrolysed ions, further studies were made of the behaviour of $[Tc_2X_8]^{3-}$ (where X = Cl, Br, or I) in solutions of hydrogen halides.[8,23,24,82] They were performed mainly in relation to the most stable and most readily synthesised $[Tc_2Cl_8]^{3-}$ ion (Fig.2); kinetic methods with optical recording were employed. The identity of the reaction products was in most cases confirmed by their isolation in the solid phase. The studies showed that the stability of the $[Tc_2X_8]^{3-}$ ions (where X = Cl, Br, or I) in aqueous solutions is determined by the sum of competing processes: acid hydrolysis, complex formation with subsequent disproportionation and dissociation of the M–M bonds, and oxidative addition of atmospheric oxygen to the Tc–Tc multiple bond. We shall consider these processes in greater detail.

(a) Acid Hydrolysis (Anation Reactions)

$$[Tc_2X_8]^{3-}+nH_2O\rightleftarrows[Tc_2X_{8-n}(H_2O)_n]^{(3-n)-}+nX^-. \qquad (3)$$

The acid hydrolysis (anation) reactions predominate when the concentration of hydrogen halide in solution is $\lesssim$3 M. They are not accompanied by the dissociation of the M–M bonds and the oxidation of the hydrolysis product by atmospheric oxygen. The final product of reaction (3) is the hydrated cluster technetium oxide $Tc_4O_5.14H_2O$ (Table 1). The tendency towards hydrolysis increases in the sequence of halogens Cl < Br < I.[11,13,23,24,82]

(b) Complex Formation

$$[Tc_2X_8]^{3-}+X^-\rightleftarrows[Tc_2X_9]^{4-}. \qquad (4)$$

The complex formation reactions predominate in concentrated hydrogen halide solutions. When the ligands are replaced in the sequence X = Cl, Br, and I, the equilibrium in reactions (4) shifts increasingly to the right. The $[Tc_2X_9]^{4-}$ ion formed under these conditions apparently no longer has an eclipsed conformation, its Tc–Tc bond is appreciably weakened, and it can readily undergo further reactions leading to the dissociation of the M–M bonds.[8,11,13,24,82]

(c) Disproportionation with Dissociation of the M–M Bond

$$[Tc_2X_9]^{4-}+X^- \rightleftarrows [Tc(II)]+[Tc(III)]. \quad (5)$$

The mononuclear technetium(II) and technetium(III) formed as a result of this reaction are unstable and undergo further rapid reversible reactions involving disproportionation, oxidation by atmospheric oxygen, and dimerisation:[13,24]

$$[Tc(II)]+[Tc(II)] \overset{HX}{\rightleftarrows} [Tc_2X_6]^{2-}; \quad (6)$$

$$[Tc(III)]+[Tc(III)] \overset{HX}{\rightleftarrows} [Tc_2X_8]^{2-}; \quad (7)$$

$$[Tc(III)]+[Tc(III)] \overset{HX}{\rightleftarrows} [TcX_6]^{2-}+[Tc(II)]; \quad (8)$$

$$[Tc(II)] \xrightarrow[HX]{O_2} [TcX_6]^{2-}; \quad (9)$$

$$[Tc(III)] \xrightarrow[HX]{O_2} [TcX_6]^{2-}. \quad (10)$$

In the absence of oxidants, for example atmospheric oxygen, an overall mobile equilibrium is established:[13,24]

$$4[Tc_2X_8]^{3-} \rightleftarrows 2[TcX_6]^{2-}+3[Tc_2X_6]^{2-}+2X^-. \quad (11)$$

Analysis of reactions (1)–(8) and (11) shows that there exists a narrow range of HX and technetium ion concentrations in which there is a possibility of a prolonged existence of $[Tc_2X_8]^{3-}$ and the limits of this range become very markedly narrower in the sequence of halogens Cl > Br > I. For example, at an initial concentration $[Tc_2Cl_8]^{3-} > 10^{-2}$ M and for ~3 M < [HCl] < ~6 M, the solutions of the octachloroditechnetate can exist indefinitely without visible changes in the absence of atmospheric oxygen, while the octaiododitechnetates decompose almost at the instant of their formation in hydriodic acid. The octabromoditechnetates, which can be obtained at a high (~1 M) concentration of technetium ions and a high temperature in the autoclave {when the autoclave is cooled, crystals of $M_3[Tc_2Br_8].nH_2O$ are precipitated and virtually only the $[TcBr_6]^{2-}$ and $[Tc_2Br_6]^{2-}$ ions remain in the mother liquor}, occupy an intermediate position.

Thus partial evaporation of HCl in the synthesis of $[Tc_2Cl_8]^{3-}$ by the method of Eakins et al[5] and by the autoclave method[6–8] creates favourable conditions (from the standpoint of the acidity and the concentration of technetium ions in solution) for the formation of the octachloroditechnetates(+2.5), since, on the one hand, the rate of reduction of the technetium(IV) ions increases owing to their hydrolysis,[7] and, on the other, the stability of the hydrolysed cluster ions formed increases in relation to the reactions involving disproportionation and oxidation by atmospheric oxygen.[13,23,24,82] We may note that, under the conditions of more pronounced hydrolysis, the rate of reduction of technetium(IV) increases so much that the formation of metallic technetium becomes possible.

3. Oxidation-reduction Reactions

In solutions with a high $[Tc_2Cl_8]^{3-}$ concentration the octachloroditechnetate ions can enter into reactions in which oxygen undergoes oxidative addition to the Tc–Tc multiple bond:[11,13,24,82]

$$[Tc_2Cl_8]^{3-}+O_2 \rightarrow [Tc_2Cl_8O_2]^{3-}. \quad (12)$$

The Tc–Tc bond in dinuclear $Tc^{4.5+}$ complexes formed is greatly weakened (Table 1) and the complexes readily decompose in HCl solutions to the mononuclear complexes of quinquevalent and quadrivalent technetium:

$$[Tc_2Cl_8O_2]^{3-} \xrightarrow{HCl} [TcO(OH)Cl_4]^{2-}+[TcCl_6]^{2-}. \quad (13)$$

In the absence of complex-forming agents and in aprotic solvents the $[Tc_2Cl_8O_2]^{3-}$ ions are comparatively stable and can be isolated in the form of the salt $K_3[Tc_2Cl_8O_2]$ (Table 1). We may note that the analogous reactions involving the addition of oxygen to the quadruple M–M bond in the $[Tc_2Cl_8]^{2-}$ complexes lead to the formation of mononuclear oxohalogenotechnetium(V) complexes even in aprotic solvents:[13]

$$[Tc_2Cl_8]^{2-}+O_2 \rightarrow [Tc_2Cl_8O_2]^{2-} \rightarrow 2[TcOCl_4]^-. \quad (14)$$

Oxidative addition reactions have been recently observed also for the dinuclear clusters of other *d* transition elements with multiple M–M bonds.[83] The multiplicity of the M–M bonds must decrease in these reactions. It is known from organic chemistry that similar reactions are extremely characteristic of unsaturated organic compounds. We believe that the capacity for oxidative addition reactions is a common property of homeopolar multiple bonds.

Apart from the reactions involving the oxidative addition of oxygen, the usual oxidation-reduction reactions have also been observed for dinuclear technetium clusters with multiple M–M bonds (in this case they must be accompanied by a change in the multiplicity of the Tc–Tc bonds up to their complete dissociation):[10,13,20,22,24]

$$[Tc_2Cl_8]^{2-} \xrightarrow[HCl]{O_2} [Tc_2Cl_8]^{3-}; \quad (15)$$

$$[Tc_2Cl_8]^{3-} \xrightarrow[-e^-]{O_2} [Tc_2Cl_8]^{2-}. \quad (16)$$

Reaction (15) is very rapid and takes place in hydrochloric acid solution. Reaction (16) is slower and is characteristic of aprotic solvents since the $[Tc_2Cl_8]^{2-}$ ions rapidly decompose in hydrochloric acid solutions via reactions of type (4)–(11). In the presence of an excess of the reductant, reactions (15) and (16) can also proceed in the reverse direction.

4. The Ligand Substitution Reaction

Three types of ligand substitution reactions are now known for technetium clusters.

(a) Reversible substitution of monodentate ligands by other monodentate ligands:[10,11,13,22,24]

$$[Tc_2Cl_8]^{2-}+8X^- \rightleftarrows [Tc_2X_8]^{3-}+8Cl^-; \quad (17)$$

$$[Tc_2Cl_8]^{2-}+8X^- \rightleftarrows [Tc_2X_8]^{2-}+8Cl^-; \quad (18)$$

$$[Tc_2Cl_8]^{2-}+8X \rightleftarrows [Tc_2X_8]^{2}+8Cl^-. \quad (19)$$

The equilibria in these reactions are strongly displaced to the right for X = Br or I. The formation of mixed complexes has not been observed.

(b) Reversible substitution of monodentate ligands by bidentate ligands (Figs.3–6):[9–11,13,18]

$$[Tc_2Cl_8]^{3-}+4CH_3COO^- \rightleftarrows [Tc_2(CH_3COO)_4Cl_2]^-+6Cl^-; \quad (20)$$

$$[Tc_2(CH_3COO)_4Cl_2]^- \overset{CH_3COOH}{\rightleftarrows} [Tc_2(CH_3COO)_4Cl]+Cl^-; \quad (21)$$

$$[Tc_2Cl_8]^{3-}+4o\text{-}C_6H_4(OH)N \rightleftarrows [Tc_2(C_6H_4ON)_4Cl]+7Cl^-+4H^+. \quad (22)$$

These reactions proceed in the forward direction only at high temperatures (~120 °C) and in the presence of an excess of the bidentate complex-forming agent, while the reverse reactions (20)–(22) take place also at room temperature in the presence of an excess of HCl.

(c) Oxidative substitution of monodentate ligands by bidentate ligands (Figs.4, 6, and 8):[10,13,17]

$$[Tc_2Cl_8]^{3-} \xrightarrow[-6Cl^-;\ -e^-]{(CH_3)_3CCOOH} \{Tc_2[(CH_3)_3CCOO]_4Cl_2\}; \qquad (23)$$

$$[Tc_2X_6]^{2-} \xrightarrow[-5X^-,\ -e^-]{CH_3COOH} [Tc_2(CH_3COO)_4X]. \qquad (24)$$

These reactions are irreversible; organic acid ions apparently behave in the reactions as oxidants, being converted into the corresponding alcohols and their esters.[13] Reactions (23) and (24) take place only at high temperatures (>150 °C) and in the presence of a large excess of organic acid.

Disproportionation reactions of type (11) with formation of $[Tc_2X_6]^{2-}$ and $[TcX_6]^{2-}$ take place simultaneously with the ligand substitution reactions (17), (18), and (20) involving the $[Tc_2X_8]^{3-}$ complexes. However, the analogous complexes with bidentate bridging ligands (the d^4–d^5 complexes with the "lantern" structure—see Figs.4–6) do not undergo disproportionation reactions.[9] This fact constitutes additional confirmation that the disproportionation of $[Tc_2X_8]^{3-}$ is accompanied by the dissociation of the Tc–Tc bond, while the bidentate bridging acetate ions stabilise these bonds. We may note that the dinuclear complexes with Tc–Tc bonds behave analogously also in thermal decomposition reactions.

5. Reactions of Polynuclear Cluster Compounds

On further reduction of the $[Tc_2X_6]^{2-}$ ions in an autoclave with molecular hydrogen under pressure in concentrated solutions of hydrogen halides, there is a possibility of cycloaddition reactions:[10,12,13]

$$n[Tc_2X_6]^{2-} \xrightarrow[-kX^-]{me^-} [Tc_{2n}X_{6n-k}]^{(2n+m-k)-}. \qquad (25)$$

Since reactions with an order greater than two are unlikely in solutions, one may postulate that reaction (25) takes place in stages, i.e. tetranuclear, hexanuclear, octanuclear, etc, technetium clusters should be formed in the $[Tc_2X_6]^{2-}$ reduction processes.

Hexanuclear and octanuclear technetium clusters of this type, which have not so far been synthesised for other *d* elements, have now been characterised by means of X-ray diffraction[76,79] (Figs.12 and 14 and Table 1). A characteristic feature of these clusters is the presence in their structure of several quadruple Tc–Tc bonds and of a system of many-centre M–M bonds. Several $[Tc_2X_2\mu\text{-}X_4]$ fragments, which are residues of the $[Tc_2X_6]^{2-}$ ions, can be readily differentiated in both structures. Since the appearance of the quintuple Tc–Tc bond (σ^2, $2\pi^2$, δ^2_{xy}, $\delta^2_{x^2-y^2}$) is most likely in the $[Tc_2X_6]^{2-}$ ions, reaction (25) may be regarded as a kind of cyclic polycondensation reaction involving the binding of the $[Tc_2X_6]^{2-}$ monomers to one another via the formation of many-centre M–M bonds with a simultaneous decrease of the multiplicity of the Tc–Tc bond in the monomers to 4.0. Some of the halogen ions are then split off from the monomers, while others become bridging species linking the monomers to one another.

One must note the similarity of these reactions to the analogous cycloaddition reactions of unsaturated organic compounds (for example, to the trimerisation of acetylene with formation of benzene). However, inorganic cycloaddition reactions are not accompanied by the initial formation of a system of conjugated equivalent M–M bonds of high multiplicity, although in the present instance there are grounds for such hypothesis. From our point of view,[13] the reason for this is the higher potential barrier for this kind of redistribution of electron density in the case of quadruple M–M bonds.

Special mention must be made of the role of unpaired electrons in inorganic cycloaddition reactions of type (25). For example, according to preliminary data,[13] the $[Tc_2X_6]^{2-}$ anions do not enter directly into reaction (25) and only the products of their one-electron reduction, which are probably the $[Tc_2X_6]^{3-}$ ions with unpaired electron, initiate these reactions. Thus monomers of the type of $[Tc_2X_6]^{3-}$ with a single unpaired electron behave, on the one hand, as analogues of organic radicals in polymerisation reactions and, on the other hand, the presence of the unpaired electron leads to the removal of the prohibition of cycloaddition reactions with thermal excitation (this conclusion follows from the theory of the conservation of orbital symmetry in cycloaddition reactions[85,86]).

A further increase of the temperature of the synthesis in the autoclave (in hydrobromic acid) leads to the formation of octahedral technetium clusters with equivalent M–M bonds (Fig.13 and Table 1) of the type of $[H_3O(H_2O)_3]_2[Tc_6Br_6\mu\text{-}(Br, OH)_6]$.[10,13] On the basis of general considerations, one can postulate that the compound is formed either directly in the cycloaddition reactions of the $[Tc_2X_6]^{n-}$ anions (where $n = 2$ or 3) or via a rearrangement of the hexanuclear or octanuclear clusters with quadruple M–M bonds which have already been formed. Thus, an unambiguous solution of the problem of the mechanism of the formation of the given octahedral cluster requires in the first place the elucidation of the form (polynuclear or dinuclear) in which the hexanuclear and octanuclear technetium clusters with quadruple M–M bonds exist in solution. Since the solubility of these compounds becomes appreciable only at a high temperature in the autoclave, the elucidation of the form in which these clusters exist in solutions of hydrogen halides involves considerable experimental difficulties.

Thus, the chemical properties of the technetium clusters are similar to those of the usual mononuclear complexes (hydrolytic reactions, reactions involving the substitution of monodentate ligands by other monodentate ligands, complex formation reactions, and oxidation-reduction processes) as well as typical polynuclear clusters of other *d* transition elements (reactions accompanied by a change in the multiplicity of the M–M bonds up to their complete dissociation and by the substitution of monodentate ligands by bidentate ligands with formation of complexes having a structure of the "lantern" type). However, some of the reactions of the dinuclear and polynuclear technetium clusters are characteristic also of unsaturated organic compounds with multiple homeopolar bonds: reactions involving oxidative addition to multiple bonds and reactions in which multiple bonds undergo cycloaddition with formation of closed cyclic systems.

In a number of cases "anomalies" were observed in the properties of technetium cluster compounds compared with the clusters of other *d* transition elements, for example an increased capacity for the formation of stable paramagnetic clusters or clusters with complex systems of M–M bonds, including several quadruple Tc–Tc bonds. Naturally one cannot exclude the possibility that these "anomalies" are caused solely by the lack of adequate experimental data on the clusters of other *d* transition elements and that in the future similar properties will be observed also for clusters

of other metals. However, it is likewise probable that by virtue of its "crossing" position in Mendeleev's Table, technetium should possess simultaneously the capacity for the formation of both dinuclear clusters with weak-field ligands and M–M bonds having a high multiplicity and polynuclear clusters with strong- and weak-field ligands. It may be that the "anomalous" properties of technetium clusters are due precisely to this factor and also the fact that the theory of clusters is as yet too inadequate to explain unambiguously and to predict all the wide variety of the properties of these compounds.

IV THERMOCHEMICAL BEHAVIOUR

The thermal stability of the dinuclear clusters has been studied in order to elucidate the mechanisms of the thermal decomposition and the composition of the intermediates, to establish the relation between composition and thermal stability, and to elucidate the possibility of obtaining metallic technetium and coatings based on it. Investigations have shown that the thermal decomposition of technetium cluster compounds is a multistage process, which depends on the composition and structural features of the initial compound. In many cases the thermal decomposition is accompanied by disproportionation into technetium(IV) and metallic technetium:[39,87]

$$K_3[Tc_2Cl_8]\cdot 2H_2O \xrightarrow{130-160^\circ} K_3[Tc_2Cl_8] + 2H_2O \xrightarrow{370-450^\circ} \rightarrow 5/4K_2[TcCl_6] + 1/2KCl + 3/4Tc; \quad (26)$$

$$K_2[Tc_2X_6]\cdot 2H_2O \xrightarrow{130-150^\circ} K_2[Tc_2X_6] + 2H_2O \xrightarrow{550-650^\circ} K_2[TcX_6] + Tc, \quad (27)$$

where X = Cl or Br. If the hexahalogenotechnetate(IV) formed initially is thermally stable, as, for example, $K_2[TcCl_6]$, it remains in the system up to 1100 °C; otherwise it undergoes further thermal decomposition:[88]

$$K_2[TcBr_6] \xrightarrow{700-750^\circ} 2KBr + 2Br_2 + Tc. \quad (28)$$

We may note that reactions (26)–(28) are characteristic solely of cluster complexes with inorganic cations. For organic cations, the thermal decomposition of the cluster can proceed by one of the following pathways:[39]

$$(PyH)_3[Tc_2Cl_8]\cdot 2H_2O \xrightarrow{130^\circ} (PyH)_3[Tc_2Cl_8] + 2H_2O \xrightarrow{250-280^\circ} \rightarrow (PyH)Cl + [Tc_2(Py)_2Cl_5] + 2HCl \xrightarrow{415^\circ} 2Tc + 2Py + {}^5/_2Cl_2; \quad (29)$$

$$[(C_2H_5)_4N]_2[Tc_2Cl_8] \xrightarrow{298-305^\circ} 2Tc + 5/2Cl_2 + 2(C_2H_5)_3N + HCl + C_2H_4. \quad (30)$$

The second stage of the thermolysis of $(PyH)_3[Tc_2Cl_8]\cdot 2H_2O$ (at 250–280 °C) proceeds via the mechanism of Andersen's reaction and is accompanied by the migration of pyridine to the inner coordination sphere of the dinuclear complex [the ν(Tc–N) are 234 and 258 cm^{-1}]. The disproportionation of the dinuclear complex is not observed at this stage and its Tc–Tc bond is retained.[39] This is indicated by infrared and ESCA spectroscopic data as well as measurements of the static magnetic susceptibility (Table 1). In the case of the mononuclear pyridinetechnetium(IV) chloride complex the migration of pyridine into the coordination of sphere of technetium consists of two stages:[89,90]

$$(PyH)_2[TcCl_6] \xrightarrow{250^\circ} (PyH)[TcPyCl_5] + HCl \xrightarrow{316^\circ} [TcPy_2Cl_4] + HCl. \quad (31)$$

The thermal decomposition of the tetraethylammonium cluster via reaction (30) takes place in one stage, but the metallic technetium formed in this process is frequently contaminated by the carbide TcC.[39]

The thermal decomposition of $K[Tc_2(CH_3COO)_4]Cl_2$ also takes place in one stage with absorption of much heat:

$$2K[Tc_2(CH_3COO)_4]Cl_2 \xrightarrow{400-460^\circ} 2KCl + 4Tc + 4(CH_3CO)_2O + Cl_2 + 2O_2. \quad (32)$$

In contrast to reactions (29) and (30), reaction (32) is relatively unsuitable for the preparation of pure metallic technetium in the laboratory, as in this case the final products contain large amounts of potassium chloride.

Studies of the thermal stability of dinuclear cluster carboxylates with a structure of the "lantern" type, not containing inorganic cations (Figs.4 and 6), are of considerable interest, since in this instance the decomposition of the complexes is preceded by a sublimation stage and the gaseous product formed decomposes to metallic technetium on the walls of the reaction vessel:[39]

$$2[Tc_2(CH_3COO)_4]Cl \xrightarrow{400-460^\circ} 4Tc + 4(CH_3COO)_2O + Cl_2 + 2O_2; \quad (33)$$

$$2[Tc_2(CH_3COO)_4]Br \xrightarrow{400-460^\circ} 4Tc + 4(CH_3COO)_2O + Br_2 + 2O_2. \quad (34)$$

The metallic technetium deposited on the walls of the reaction vessel is not contaminated by solid extraneous impurities. When the conditions are chosen appropriately, this method can be used to prepare technetium coatings which nowadays can be of great practical importance, in the preparation of sources of β-radiation for radiography[91] and also of anti-corrosion materials and materials resisting surface growth.[92]

Thus the data presented in the review permit the conclusion that technetium is one of the most powerful cluster forming agents: in the lowest oxidation states it is characterised by a tendency towards the formation of dinuclear and polynuclear clusters with both strong-field and weak-field ligands and M–M bonds of different multiplicity. The properties of the technetium clusters are closest to those of the analogous rhenium and molybdenum compounds.[1-4,32-34,93-106] However, there are also certain unusual properties. In the first place there is an increased tendency towards the formation of stable paramagnetic dinuclear and polynuclear clusters with a single unpaired electron in one of the antibonding "metallic" MO. The presence of this electron leads to the additional stabilisation of the technetium clusters. This phenomenon has been observed also for the clusters of other *d* elements, but in technetium it is more pronounced owing to the reduction of the effective charge on its atoms on formation of M–M bonds. Such reduction of Z_{eff} is responsible for the appearance in technetium of an increased tendency towards the formation of different types of cluster compounds with weak-field ligands which are readily interconverted. By virtue of this property, polynuclear clusters belonging to a new class with a complex system of M–M bonds, including several quadruple or triple Tc–Tc bonds, have been obtained for the first time for technetium. The polynuclear technetium clusters have an excess of electrons and are of interest for experimenters and theoreticians.

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Phosphinepalladium and Phosphineplatinum Carbonyl Cluster Compounds

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The state of the chemistry of the cluster compounds of palladium and platinum is examined. The principal properties, structure, chemical reactions, and methods of synthesis of the phosphinepalladium and phosphineplatinum carbonyl clusters are described and the methods used to regulate the nuclearity of the clusters and their interconversions are discussed. The bibliography includes 69 references.

CONTENTS

I. Introduction 394
II. Types of phosphinepalladium and phosphineplatinum carbonyl clusters 394
III. The interconversions of phosphinepalladium carbonyl clusters 402
IV. Chemical properties 404

I. INTRODUCTION

Several classifications of the cluster compounds of metals are available at the present time,[1] but the phosphinemetal carbonyl clusters have not been differentiated into an independent group in any of them. This is justified in relation to the phosphinemetal carbonyl clusters for metals belonging to the Fe and Cl triads, which are merely modifications of the corresponding carbonyl compounds obtained by substituting some of the CO groups by tertiary phosphines. However it does not apply to phosphinemetal carbonyl clusters of metals belonging to the Ni triad, which have no corresponding neutral carbonyl precursors and which have a unique intrinsic structure.

The stability of a cluster with a specific number of metal atoms n is determined by a fairly fine balance between the number of the valence electrons belonging to the metallic framework proper, the number of electrons supplied by the ligands, and the steric characteristics of the ligands. The clusters of metals having a large number of valence electrons (Ni, Pd, Pt, Au) are able to coordinate the smallest number of ligands in the clusters of preceding transition metals, which leads, for comparable dimensions of the metallic framework, to an incomplete filling of the surface of the framework by ligands and an inadequate steric stabilisation of the cluster. Tertiary phosphines as ligands are isoelectronic with carbon monoxide and, for the same number of valence electrons introduced into the cluster molecule, ensure a more effective shielding of the surface of the metallic framework. We believe that this is the explanation of the transition from the neutral purely carbonyl clusters of the Fe and Co triads to the phosphinepalladium and phosphineplatinum carbonyl clusters and the phosphinegold clusters. In other words, just as carbonyl clusters are typical for the Fe and Co triads, the phosphinemetal carbonyl clusters are typical for platinum and palladium and characterise the capacity of these metals for cluster formation. The phosphinemetal carbonyl clusters examined in this review are not the only palladium and platinum clusters. There exist a series of clusters of these metals with a wide variety of ligands: $[Pd_4(CO)_4(OAc)_4]$,[2] $[Pd_4(phen)_4(CO)_2](OAc)_4$,[3] $[Pd_3(SO_2)_2.CNBu)_5]$,[4] $[Pd_3(\mu\text{-}Cl)(\mu\text{-}PPh_2)_2(PEt_3)_3]BF_4$,[5] $[Pt_3(CNBu_6]$,[6] $[Pt_3(\mu\text{-}SO_2)_3(PPh_3)_3]$,[7,8] $[Pt_3(Ph)(\mu\text{-}PPh_2)_2(PPh_3)_3]$,[9] $[Pt_3(\mu\text{-}Ph)(\mu\text{-}PPh_2)(\mu\text{-}SO_2)(PPh_3)_3]$,[10] $[Pt_3(cod)_3(\mu_3\text{-}SnCl_3)_2]$,[11] $[Pt_4(OAc)_8]$,[12] $[Pt_5H_8P(t\text{-}Bu_2Ph)_5]$,[13] [$Pt_7$(2,6-xylyl isocyanide)$_{12}$],[14] and $[Pd_3(\mu\text{-}CO)(dppm)_3]^{2+}$,[18] where phen = phenanthroline, cod = cyclo-octa -1,5-diene, and dppm = bis(diphenylphosphino)methane.

It is noteworthy that, apart from the series of anionic platinum carbonyls i.e. $[Pt_3(\mu\text{-}CO)_3(CO)_3]_n^{2-}$ (n = 1, 2, 3, 4, 5, 6),[15,16] $[Pt_{19}(CO)_{22}]^{4-}$, $[Pt_{26}(CO)_{32}]^{2-}$, and $[Pt_{38}.(CO)_{44}H_2]^{2-}$,[17] investigated by Chini and co-workers, the majority of the remaining compounds are represented in the literature by single examples and are not discussed in this review. The structures, physicochemical properties, and reactivities of neutral phosphinepalladium and phosphineplatinum carbonyl clusters are examined below in succession.

II. TYPES OF PHOSPHINEPALLADIUM AND PHOSPHINEPLATINUM CARBONYL CLUSTERS.

1. The Trinuclear Clusters $M_3(CO)_3L_3$

Clusters having this composition are known mainly for bulky ligands [L = P(t-Bu)$_3$, PPh(t-Bu)$_2$, and P(cyclo-C_6H_{11})$_3$ (Table 1)]. The method of their synthesis is based on the interaction of coordination-unsaturated compounds of the type of PdL_2 or PtL_2 with carbon monoxide; intermediate phosphinemetal carbonyl complexes are formed and are then converted into the $M_3(CO)_3L_3$ clusters. The reaction is rapid and the yields of the desired products are high (>90%). In certain cases hydride complexes were used as the starting compounds:[23-25]

$$3PtH_2[P(t\text{-}Bu)_3]_2 \xrightarrow{CO} \{Pt(CO)[P(t\text{-}Bu)_3]\}_3 + 3P(t\text{-}Bu)_3 + 3H_2;$$

$$3\{PtH(\mu\text{-}H)[P(t\text{-}Bu)_3]\}_2 \xrightarrow{CO} 2\{Pt(CO)[P(t\text{-}Bu)_3]\}_3 + 3H_2;$$

$$3\ trans\text{-}[PtH(NH_3)(PR_3)_2]^+ \xrightarrow[acetone]{CO} [Pt_3(CO)_3(PR_3)_3] + 3NH_4^+;$$

$$PR_3 = P(t\text{-}Bu)_3, PPh(t\text{-}Bu)_2.$$

X-Ray diffraction analysis has been carried out for the compound $Pt_3(CO)_3[P(cyclo\text{-}C_6H_{11})_3]_3$.[26] The metallic skeleton of the cluster has the form of an equilateral triangle all the sides of which are spanned by bridging CO groups (Fig.1); the phosphorus atoms are located in the plane of the triangle.

The D_{3h} symmetry of these compounds is also confirmed by ^{31}P and ^{195}Pt NMR data for the $Pt_3(CO)_3[P(cyclo\text{-}C_6H_{11})_3]_3$ cluster in solution.[21] The presence of the ^{31}P and ^{195}Pt nuclei in the cluster ensures that the NMR spectra yield much information and a virtually unambiguous interpretation of the structure of the compound in solution. Since the content of the ^{195}Pt isotope is 33.7% in natural compounds,

the ^{31}P spectrum consists of a superposition of the spectra of the three isotopomers (A), (B), and (C), while the ^{195}Pt spectrum consists of a superposition of two such isotopomers, namely (B) and (C) (Fig. 2). The content of the isotopomer with three magnetic platinum nuclei is low (3.70%) and the isotopomer is not manifested in the spectra. The observed spin–spin coupling constants are listed in Table 2.

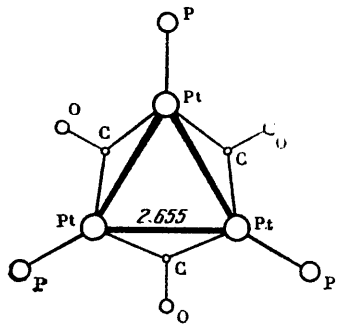


Figure 1. The structure of the $Pt_3(CO)_3[P(cyclo\text{-}C_6H_{11})_3]_3$ cluster.[26]

A more complex pattern is observed in the infrared spectra of the compounds investigated. The stretching vibrations of the CO groups in the phosphinemetal carbonyl clusters are clearly shown in the infrared spectra, which can serve as a basis for structural analysis. According to the D_{3h} symmetry, a single ν(CO) band should be observed in the spectra of these compounds. However, the data obtained (Table 3) indicate a more complex character of the spectra. In most cases two bands are observed in the ν(CO) region and for palladium compounds even three bands are found. Such increase in the complexity of the spectra of the $M_3(CO)_3L_3$ clusters is associated with the influence of a number of factors (dissociation, change in nuclearity, etc.). It is noteworthy that in the description of the infrared spectroscopic data only the solvent is usually indicated and the influence of the gas phase (inert gas, CO, air), which is insignificant in the case of trinuclear clusters, is disregarded.[27] This is probably one of the causes of the conflicting infrared spectroscopic data.

Table 1. The synthesis of phosphinemetal carbonyl clusters $M_3(CO)_3L_3$ and $M_3(CO)_3L_4$.

Cluster	Initial compound	M:P*	Conditions of synthesis	Refs.
$Pd_3(CO)_3[P(t\text{-}Bu)_3]_3$	$Pd[P(t\text{-}Bu)_3]_2$	1:2	Hexane, CO	[19]
$Pd_3(CO)_3[P(t\text{-}Bu)_2Ph]_3$	$Pd[P(t\text{-}Bu)_2Ph]_2$	1:2	Hexane, CO	[19]
$Pt_3(CO)_3[P(t\text{-}Bu)_3]_3$	$Pt[P(t\text{-}Bu)_3]_2$	1:2	Hexane, CO	[20]
$Pt_3(CO)_3[PPh(t\text{-}Bu)_2]_3$	$Pt[PPh(t\text{-}Bu)_2]_3$	1:2	Hexane, CO	[19]
$Pt_3(CO)_3[P(cyclo\text{-}C_6H_{11})_3]_3$	$PtHCl[P(cyclo\text{-}C_6H_{11})_3]_2$	1:2	Ethanol, KOH, CO	[21]
$Pt_3(CO)_3[P(Ph_2Bz)]_3$	K_2PtCl_4	1:2	Ethanol, KOH, CO	[22]
$Pt_3(CO)_3[P(iso\text{-}Pr)_3]_3$	*trans*-$PtHCl[P(iso\text{-}Pr)_3]_2$	1:2	Ethanol, KOH, CO	[21]
$Pt_3(CO)_3[PPh(iso\text{-}Pr)_2]_3$	$Pt(cod)_2$	1:1	Petroleum ether, CO	[21]
$Pd_3(CO)_3(PPh_3)_4$	$PdCl_2(PPh_3)_2$	1:2	Aniline, methanol, CO	[28]
$Pd_3(CO)_3(PPh_3)_3$	$Pd(OAc)_2$	1:2	Acetone, CO, NaOAc	[29]
$Pd_3(CO)_3[P(C_6H_4\text{-}p\text{-}CH_3)_3]_4$	$Pd(OAc)_2$	1:2	Acetone, CO, NaOAc	[29]
$Pd_3(CO)_3[P(C_6H_4\text{-}p\text{-}OCH_3)_3]_4$	$Pd(OAc)_2$	1:2	Acetone, CO, NaOAc	[29]
$Pt_2(CO)_2(PPh_3)_4$	$Pt(CO)_2(PPh_3)_2$	1:2	Ethanol	[22]
$Pt_3(CO)_3(PEt_3)_4$	$Pt_4(CO)_5(PEt_3)_4$	1:1,3	Hexane, methanol	[30]
$Pt_3(CO)_3(PPhMe_2)_4$	*cis*-$[PtCl_2(PPhMe_2)_2]$	1:2	Methanol, KOH, CO	[31]
$Pt_3(CO)_3(PPh_2Et)_4$	K_2PtCl_4	1:2	Methanol, KOH, CO	[22]
$Pt_3(CO)_3(PPh_2Me)_4$	Na_2PtCl_4	1:2	Methanol, KOH, CO	[22]
$Pt_3(CO)_3[PEt_2(cyclo\text{-}Bu)]_4$	$Pt(cod)_2$	1:1,6	Petroleum ether, CO	[31]
$Pt_3(CO)_3[P(cyclo\text{-}C_6H_{11})_3]_4$	$PtH_2[P(cyclo\text{-}C_6H_{11})_3]_2$	1:2	Hexane, CO	[32]
$Pt_3(CO)_3(PPh_2Bz)_4$	$Pt_3(CO)_3(PPh_2Bz)_3$	1:1,5	Diethyl ether	[31]

*The M : P molar ratio used in the synthesis is quoted.

Table 2. ^{31}P and ^{195}Pt NMR data for the $Pt_3(CO)_3L_3$ clusters.

Ligand	δ(P), p.p.m.	δ(Pt), p.p.m.	^1J (Pt, Pt)	^1J (Pt, P)	^2J (Pt, P)	^3J (P, P)	Refs.
P(cyclo-C_6H_{11})3	69.8	—4392	1571	4412	430	58	[21]
P(iso-Pr)3	81.6	—4530	1607	4422	419	56	[21]
P(iso-Pr)2Ph	76.7	—4450	1610	4605	453	57	[21]
PPh_2Bz	55.6	—4448	1619	4751	488	63	[21]
P(t-Bu)$_2$Me	68.4	—	1770	4724	413	51	[44]
P(t-Bu)Et$_2$	73.8	—4445	1595	4430	435	59	[31]

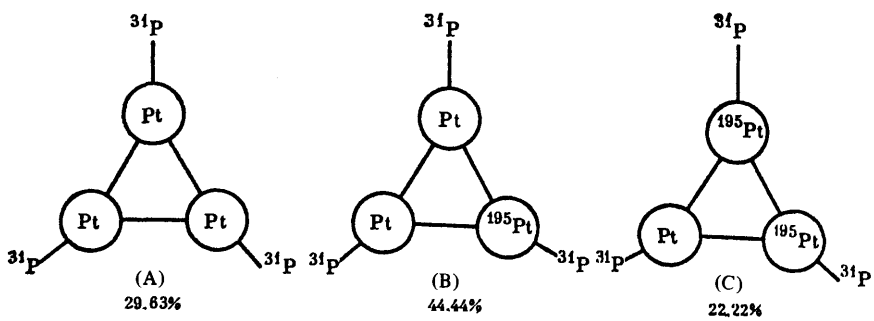


Figure 2. Principal types of the isotopomers of the $Pt_3(CO)_3L_3$ cluster.

2. Trinuclear $M_3(CO)_3L_4$ Clusters

This group of clusters is known for a fairly large number of ligands (Table 1). The trinuclear palladium clusters† are obtained by reducing $PdCl_2L_2$ with carbon monoxide (L = PPh_3) or by reducing $Pd(OAc)_2$ in the presence of NaOAc and two equivalents of a phosphine ligand [L = PPh_3, $P(C_6H_4\text{-}p\text{-}CH_3)_3$, or $P(C_6H_4\text{-}p\text{-}OCH_3)_3$]. The trinuclear platinum clusters were obtained by the following procedures:

(a) by treating the compound $Pt(cod)_2$ with phosphine and carbon monoxide. A solution of $Pt(cod)_2$ in petroleum ether is treated with carbon monoxide for approximately 0.5 h after adding the phosphine [L = PEt_3, $PMePh_2$, $PEt_2(t\text{-}Bu)$, or PPh_2Bz] and the solvent is then distilled off and the required product is extracted from the residue; the yield is 50%.[31]

(b) By reducing sodium tetrachloroplatinite. A solution of Na_2PtCl_4 is treated with the phosphine and is boiled until the complete precipitation of $PtCl_2L_2$, after which is it treated with hydrazine hydrate and saturated with carbon monoxide. A solution of KOH is then introduced, the reaction mixture is again heated, boiled, and filtered. This procedure leads to the formation of the complex $Pt^0(CO)_2L_2$, which is subsequently converted on heating into the $Pt_3(CO)_3L_4$ cluster (L = PPh_3, $PMePH_2$, or $PEtPh_2$). The yield of the required product is usually 20–40%.[22]

(c) By the interaction of platinum dicarbonyl with phosphines. A solution of Na_2PtCl_4 in acetone, alcohol, or another organic solvent is treated at room temperature with carbon monoxide for 1–2 days. After the formation of platinum dicarbonyl, concentrated ammonia is added, whereupon the solution becomes bright green and capable of reacting with phosphine. When an aromatic phosphine is added to the alcoholic solution, the precipitation of the $Pt_3(CO)_3L_4$ cluster, where L = PPh_3, $P(C_6H_4\text{-}p\text{-}CH_3)_3$, $P(C_6H_3\text{-}p\text{-}OCH_3)_3$, or PPh_2Et, begins immediately. The yield of the product after recrystallisation is approximately 50%. The reaction with straight-chain aliphatic phosphines takes place nonselectively and admixtures are formed, causing rapid decomposition of the required product.[30]

Among more specific methods of synthesis, mention may be made of the interaction of carbon monoxide with $PtH_2[P(cyclo\text{-}C_6H_{11})_3]_2$ under normal conditions[32] and with $PtMe_2(PEt_3)_2$ at 90 °C and 50 atm.[37] However, in the latter case no detailed description of the method of synthesis is available in the literature.

The structure of clusters of the type $M_3(CO)_3L_4$ has been established by X-ray diffraction for $Pd_3(CO)_3(PPh_3)_4$[33] and $Pt_3(CO)_3[P(cyclo\text{-}C_6H_{11})_3]_4$.[32] The cluster molecule is an equilateral triangle all the sides of which are spanned by μ-CO groups. Each of the two metal atoms in the base of the triangle is linked to one of the two phosphorus atoms of the phosphine ligand, while the third metal atom is linked to two other phosphorus atoms (Fig.3).

The non-equivalence of the CO groups in the cluster is reflected in the infrared spectra (Table 4). In the stretching region of the μ_2-CO groups two intense bands are usually observed at 1820–1880 cm^{-1} for the palladium compounds and at 1750–1800 cm^{-1} for the platinum compounds. We may note that the infrared spectra are to a large extent characteristic and can be used to identify the clusters.

† The methods of synthesis of the $Pd_3(CO)_3(PPh_3)_4$, Pd_4, Pd_{10} clusters, based on the interconversions of the phosphinepalladium carbonyl clusters, are examined below in Section III.

The platinum clusters have been investigated by the NMR method. The ^{31}P and ^{195}Pt NMR data agree with the results of the X-ray diffraction analysis.[32] Two types of P and Pt atoms are manifested in the spectra (Table 5) and the splitting of their signals by neighbouring atoms and the number of components of the spectrum indicate a triangular skeleton in which one platinum atom is linked to two phosphorus atoms and the two others are involved in only a single Pt–C bond.

Table 3. Infrared spectroscopic data for the $M_3(CO)_3L_3$ clusters.

Ligand	ν(CO), cm^{-1}	Solvent	Refs.
	M=Pd		
$P(t\text{-}Bu)_3$	1843 s, 1802 s, 1795 s	LP	[19]
$P(t\text{-}Bu)_2Ph$	1870 s, 1832 v.s, 1820 v.s	LP	[19]
	M=Pt		
$P(t\text{-}Bu)_3$	1875 s, 1730 s	LP	[20]
$P(t\text{-}Bu)_3$	1785 s, 1730 s	CH_2Cl_2	[20]
$P(t\text{-}Bu)_3$	1792, 1740		[23]
$P(t\text{-}Bu)_2Ph$	1872 s, 1760 v.s	LP	[19]
$P(t\text{-}Bu)_2Ph$	1836 w, 1773 v.s	THF	[19]
$P(C_6H_{11})_3$	1840 w, 1770 v.s 1737 w	LP	[21]
PPh_2Bz	1784 s	LP	[22]
PPh_2Bz	1852 w, 1789 s	THF	[22]
PPh_2Bz	1855 w, 1795 s, 1788 s, 1760 sh 1750 sh	–	[21]
$P(iso\text{-}Pr)_3$	1838 w, 1770 v.s, 1738 sh	LP	[21]
$P(iso\text{-}Pr)_2Ph$	1865 w, 1800 s, 1785 s, 1760 sh	LP	[21]
$P(iso\text{-}Pr)_2Ph$	1865 w, 1805 s, 1798 sh, 1788 s 1764 v.s	C_6H_{14}	[21]

Notation: (here and henceforth): v.s. = very strong (intense), s = strong (intense), m = medium, w = weak, sh = shoulder, b = broad, and LP = liquid paraffin.

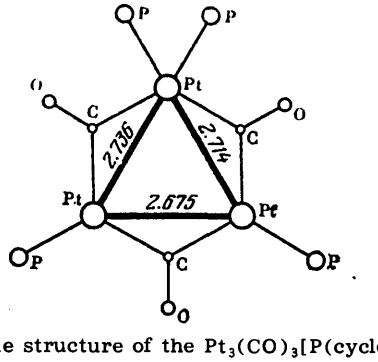


Figure 3. The structure of the $Pt_3(CO)_3[P(cyclo\text{-}C_6H_{11})_3]_4$ cluster.[32]

3. Tetranuclear $M_4(CO)_5L_4$ Clusters

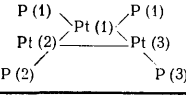
The conditions for the preparation of the tetranuclear palladium clusters (Table 6) are different for straight-chain aliphatic and triphenylphosphine ligands although $Pd(OAc)_2$ is used as the starting compound in both cases. The $Pd_4(CO)_5(PPh_2Me)_4$ palladium cluster[39] has been obtained by reducing $Pd(NO_2)_2(PPh_2Me)_2$ with carbon monoxide in

methylene chloride. The attempts to obtain the corresponding clusters with the PPh_3 and $PPhMe_2$ ligands by this reaction proved unsuccessful.

Table 4. Infrared spectroscopic data for the $M_3(CO)_3L_4$ clusters.

Ligand	ν(CO), cm^{-1}	Solvent	Refs.
	M=Pd		
PPh_3	1840, 1820	KBr	]33, 35]
PPh_3	1865 s, 1822 vs, 1790 vw	LP	[29]
$P(C_6H_4$-p-$CH_3)_3$	1879 w-m, 1846 s, 1925 vs	LP	[29]
$P(C_6H_4$-p-$OCH_3)_3$	2035 s.w, 1880 vw, 1843 s 1831 vs	LP	[29]
	M=Pt		
PPh_3	1854 w, 1803 s, 1788 s	LP	[22]
PPh_3	1845 w, 1799 s, 1782 s	LP	[34]
PPh_3	1839 m, 1784 s	Benzene	[22]
PPh_3	1854 w, 1805 sh, 1795 s	THF	[36]
PEt_3	1808 w, 1760 vs, 1745 sh	LP	[31]
PEt_3	1766 s, 1773 sh	C_6H_{14}	[37]
PEt_3	1766 s	C_6H_{14}	[38]
PEt_3	1766 s, 1774 sh, 1826 w,	C_6H_{14}	[30]
$PPhMe_2$	1825 w, 1772 vs, 1750 vs	LP	[31]
PPh_2Et	1788 s, 1765 s,	LP	[22]
PPh_2Et	1835 w, 1782 sh, 1770 s	Benzene	[22]
PPh_2Et	1849 w, 1768 s	THF	[36]
PPh_2Me	1840 w, 1792 vs, 1772 vs	LP	[31]
PPh_2Me	1847 w, 1796 s, 1769 s	LP	[22]
PPh_2Me	1839 m, 1775 s	Benzene	[22]
P(t-Bu)Et_2	1822 w, 1760 sb, 1752 sh	LP	[31]
$P(C_6H_{11})_3$	1825 w, 1780 s, 1760 s	LP	[32]
PPh_2Bz	1785 sh, 1765 sb, 1735 wb	LP	[31]

Table 5. ^{31}P and ^{195}Pt NMR data for the $Pt_3(CO)_6L_4$ clusters[31]



Parameters of spectrum	Ligand				
	PEt_3	PMe_2Ph	$PMePh_2$	PEt_2(t-Bu)	PPh_2Bz
δP(1), p.p.m.	33.7	8.8	24.5	47.0	43.8
δP(2), p.p.m.	60.8	35.6	49.8	82.5	60.0
δPt(1), p.p.m.	—3908	—3760	—3828	—3836	—3855
δPt(2), p.p.m.	—3883	—3949	—3970	—3758	—4066
^1J[Pt(1), Pt(2)], Hz	586	507	—	385	—
^1J[Pt(2), Pt(3)], Hz	1830	1840	—	1808	—
^1J[Pt(1), P(1)], Hz	3621	3611	3651	3741	3615
^1J[Pt(2), P(2)], Hz	4463	4643	4614	4317	4348
^2J[Pt(1), P(2)], Hz	445	487	519	440	455
^2J[Pt(2), P(1)], Hz	272	292	282	270	272
^2J[Pt(2), P(3)], Hz	411	427	453	459	453
^3J[P(2), P(3)], Hz	65	65	68	70	60
^3J[P(1), P(2)], Hz	21	21	21	25	20

The tetranuclear platinum clusters have been obtained mainly by two methods (Table 6).

(a) By the disproportionation of the trinuclear clusters in carbon monoxide involving the dissolution of the compound $Pt_3(CO)_3L_4$ in acetone and its maintenance in an atmosphere of carbon monoxide for several days. Crystals of the $Pt_3(CO)_5L_4$ clusters are gradually segregated (they are usually black). The synthesis can be carried out in a different way from Na_2PtCl_4. A solution of $Pt_3(CO)_3L_4$ is obtained initially, as described above, and is then kept in an atmosphere of carbon monoxide:[22]

$$2[Pt_3(CO)_3L_4] + 3CO \xrightarrow[1\ atm]{25^\circ C} Pt_4(CO)_5L_4 + 2PtL_2(CO)_2$$
$$L=PPh_3,\ PMe_2Ph,\ PPh_2Bz$$

The yield of the product ranges from 20 to 50%.

(b) By the interaction of platinum dicarbonyl with phosphines. A solution of platinum dicarbonyl obtained by the method of Eremenko et al.[30] readily reacts with straight-chain aliphatic phosphines in equimolar proportions; the $Pt_4(CO)_5L_4$ cluster is formed in a high yield (>80%):[30]

$$[Pt_3(CO)_6]_n^{2-} + PEt_3 \rightarrow Pt_4(CO)_5(PEt_3)_4$$

Table 6. The synthesis of phosphinemetal carbonyl clusters $M_4(CO)_5L_4$

Cluster	Initial compound	M:P in synthesis	Conditions of synthesis	Refs.
$Pd_4(CO)_5(PPh_2Me)_4$	$Pd(NO_2)_2(PPh_2Me)_2$	1:2	CH_2Cl_2	[39]
$Pd_4(CO)_5(PPh_3)_4$	$Pd(OAc)_2$	1:1.3	Et_2NH	[29]
$Pd_4(CO)_5(PPh_3)_4$	$Pd(OAc)_2$	1:2	Acetone, NaOAc, CO; CO + O_2 mixture	[29]
$Pd_4(CO)_5(PEt_3)_4$	$Pd(OAc)_2$	1:1÷1:2	Acetone, NaOAc, HOAc	[40]
$Pd_4(CO)_5(PBu_3)_4$	$Pd(OAc)_2$	1:1÷1:2	Acetone, NaOAc, HOAc	[40]
$Pd_4(CO)_5[P(n\text{-}C_8H_{17})_3]_4$	$Pd(OAc)_2$	1:1	Acetone, NaOAc, HOAc	[41]
$Pd_4(CO)_5[P(n\text{-}C_{12}H_{25})_3]_4$	$Pd(OAc)_2$	1:1	Acetone, NaOAc, HOAc	[41]
$Pt_4(CO)_5(PEt_3)_4$	$[Pt_3(CO)_6]_n^{2-}$	1:1	Acetone, CO	[30]
$Pt_4(CO)_5(PPhMe_2)_4$	Na_2PtCl_4	1:2	Methanol, CO, KOH, Hydrazine	[42]
$Pt_4(CO_5)(PPh_3)_4$	$Pt_3(CO)_3(PPh_3)_4$	1:1.33	Acetone, CO	[22]
$Pt_4(CO)_2(\mu\text{-dppm})$ (dppm-O)	$[Pt_2H_2(\mu\text{-H})(\mu\text{-dppm})_2][PF_6]$	—	—	[43]

The interaction of $[Pt_3(CO)_6]_n^{2-}$ for aromatic phosphine ligands has been mentioned, but a detailed description of the experiment is not available.[22]

The formation of the tetranuclear platinum cluster in the catalytic conversion of carbon monoxide should be noted:[43]

$$[Pt_2H_2(\mu\text{-H})(\mu\text{-dppm})_2]PF_6 \xrightarrow[O_2]{P_{CO}} Pt_4(\mu\text{-CO})_2(\mu\text{-dppm})_3[dppm(:O)]$$

X-Ray diffraction studies have been carried out for four compounds: $Pd_4(CO)_5(PPh_2Me)_4$,[39] $Pd_4(CO)_5(PPh_3)_4$,[33] $Pt_4(CO)_5(PMe_2Ph)_3$,[42] and $Pt_4(CO)_2(\mu\text{-dppm})_3[dppm(:O)]$.[43] Fig. 4 illustrates the structure of the $Pt_4(CO)_5(PEt_3)_4$ cluster. Its metallic skeleton has the form of a "butterfly" or an open tetrahedron. All five M–M bonds in the cluster are spanned by μ-CO groups and each metal atom is coordinated to one phosphorus atom. The remaining compounds have analogous structures. A cluster with dppm as the bridging ligand has shorter Pt–Pt bonds owing to the chelating influence of dppm.

The structure of the tetranuclear phosphineplatinum carbonyl clusters in solution was investigated by ^{31}P and ^{195}Pt NMR. If the "butterfly" structure of the $Pt_4(CO)_5(PEt_3)_4$ is retained in solution, two types of Pt nuclei with different chemical shifts should be manifested in the NMR spectrum, making it asymmetric. Experiments showed[45] that the $^{31}P\{^1H\}$ NMR spectrum of the $Pt_4(CO)_5(PEt_3)_4$ cluster is symmetrical relative to the central intense line with δ = 36.4

p.p.m., which made it possible to postulate a tetrahedral structure of the cluster in solution. Within the framework of this model, it was possible to interpret the observed spectrum as the sum of the contributions due to clusters containing between zero and four nuclei of the ^{195}Pt magnetic isotope.[45]#

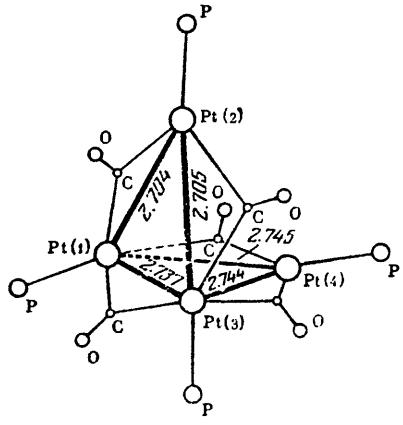


Figure 4. Structure of the $Pt_4(CO)_5(PEt_3)_4$ cluster (the X-ray diffraction analysis has been carried out by R.F.Klevtsova of the Institute of Inorganic Chemistry of the Siberian Division of the USSR Academy of Sciences).

The ^{195}Pt NMR spectrum also indicates a tetrahedral structure of the cluster (a doublet of quartets, which is a superposition of the spectra of clusters with two and three magnetic nuclei, is observed). The observed increase of the symmetry of the clusters in solution at room temperature can be explained by the stereochemical non-rigidity of the compound associated with the rapid exchange of carbonyl groups. The exchange processes remain fairly rapidly at temperatures down to -70 °C.[45]

Exchange processes have been observed for the first time also for palladium clusters whose ^{31}P NMR spectra consist of singlets—δ, p.p.m. (in benzene): -14.0 (Et) and -6.5 (Bu);[40] δ, p.p.m. (in hexane): -6.6 ($n-C_8H_{17}$) and -6.8 ($n-C_{12}H_{25}$)[45] (downfield chemical shifts relative to the H_3PO_4 signal correspond to the negative values).

Another cause of the transition to the tetrahedral structure of the Pt_4 cluster in solution may be associated with the addition of a sixth CO molecule from the solution. This possibility has been confirmed indirectly by the synthesis of the $Pd_4(CO)_6(PBu_3)_4$ cluster on slow crystallisation of $Pd_4(CO)_5(PBu_3)_4$ in a CO atmosphere.[46]

The infrared spectra of palladium compounds in the region of the stretching vibrations of the CO group are characterised by a single intense band; an intense band with a shoulder has also been observed for platinum clusters (Table 7).

A study has been published (A.Moor, P.S.Pregosin, L.M.Venanzi, and A.J.Welch, Inorg.Chim.Acta, 1985, 85, 103), whose NMR data agree with those of Yudanov et al.[45]

4. Pentanuclear $Pt_5(CO)_6L_4$ Clusters

The pentanuclear platinum clusters have been discovered recently. They have been synthesised by a fairly specific method (Table 8) involving the reduction of platinum(II) by metal carbonyl anions. For this purpose, a solution of $PtCl_2L_2$ in tetrahydrofuran was treated with $NaMn(CO)_5$ or $KFe(CO)_3NO$ and the reaction mixture was kept at room temperature (for 1 h for PEt_3 or 18 h for PPh_3). The reaction products were isolated chromatographically. The yield depends greatly on the nature of the carbonylate ion and the phosphine ligand; it amounts to 35% for PPh_3 and 50% for PEt_3 in the case of $NaMn(CO)_5$ and to 10% for PPh_2Me and 75% for PPh_3 in the case of $KFe(CO)_3NO$.[49]

Table 7. Infrared spectroscopic data for the $M_4(CO)_5L_4$ clusters.

Ligand	ν(CO), cm^{-1}	Solvent	Refs.
	M=Pd		
PPh_2Me	1840 s, 1820 sh	KBr	[39]
PPh_3	1858 s	LP	[29]
PEt_3	2018 vw, 1889 m, 1874 w 1844 s, 1797 sh	LP	[40]
PBu_3	2012 vw, 1886 w, 1851 sh, 1837 s, 1800 sh	LP	[40]
$P(n-C_8H_{17})_3$	2014 w-m, 1894 w, 1880 vw 1852 sh, 1842 sb, 1804 sh	Hexane film	[41]
$P(n-C_{12}H_{25})_3$	2012 s, 1887 w, 1852 sh, 1841 sb 1799 sh	Hexane film	[41]
	M=Pt		
PEt_3	1804 sh, 1790 s	Hexane, LP	[30]
PPh_2Me_2	1800 s, 1779 s	LP	[22]
PPh_3	1810 sh, 1797 s	LP	[22]
$Pt_3(CO)_2(dppm)_3$	1835, 1735	LP	[43]

Table 8. The synthesis of the phosphineplatinum carbonyl clusters $Pt_5(CO)_6L_4$.

Cluster	Initial compound	Pt:P*	Conditions of synthesis	Refs.
$Pt_5(CO)_6(PEt_3)_4$	$[PtCl_2(PEt_3)_2]$	1:2	$NaMn(CO)_5$	[47]
$Pt_5(CO)_6(PPh_3)_4$	$[PtCl_2(PPh_3)_2]$	1:2	$NaMn(CO)_5$	[47]
$Pt_5(CO)_6[P(C_6H_4\text{-}p\text{-}CH_3)_3]_4$	$[Pt_3(CO)_6]_n^{2-}$	1:1	Acetone, CO	[48]
$Pt_5(CO)_6[P(C_6H\text{-}p\text{-}OCH_3)_3]_4$	$[Pt_3(CO)_6]_n^{2-}$	1:1	Acetone, CO	[48]
$Pt_5(CO)_6(PPh_2Et)_4$	$[Pt_3(CO)_6]_n^{2-}$	1:1	Acetone, CO	[48]
$Pt_5(CO)_6(PBu_3)_4$	$[Pt_3(CO)_6]_n^{2-}$	1:1	Acetone, CO	[48]

*The Pt : P molar ratio in the synthesis is quoted.

A more effective and simple method of synthesis is based on the interaction of platinum dicarbonyl with phosphine.[36] A solution of platinum dicarbonyl, obtained as described above, is treated with phosphine in the proportions Pt : L = 5 : 4 and is allowed to stand for 10–15 h. The solvent is then distilled off and the product recrystallised from benzene–heptane, acetone–ethanol, etc. mixtures.

The reaction is fairly selective and takes place equally readily with aliphatic and aromatic phosphine. The yield of the product is usually high (80%). A method based on the increase of the nuclearity of the $Pt_3(CO)_3L_4$ clusters when they are deposited on different carriers is also of interest.

It has been suggested that the process procees on acid centres, since an analogous enlargement of the framework has been observed on treating the initial cluster with a 48% solution of HBF_4 in THF.[50]

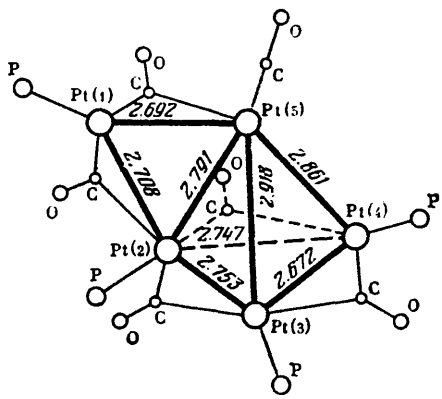


Figure 5. The structure of the $Pt_5(CO)_6(PPh_3)_4.3C_6H_6$ cluster.[48]

Table 9. Infrared spectroscopic data for the $Pt_5(CO)_6L_4$

Ligand	ν(CO), cm^{-1}	Solvent	Refs.
PPh_3*	1998 vs, 1893 w, 1854 s, 1814 s, 1790 vs	KBr	[47]
PPh_3	2005 vs, 1898 w, 1864 m, 1818 s, 1795 s	THF	[47]
PPh_3	1998 vs, 1899 m, 1858 s, 1812 s, 1788 vs	LP	[47]
PPh_3	1999 s, 1895 w, 1864 m, 1816 s, 1792 s	THF	[48]
PEt_3	1985 vs, 1880 m, 1850 s, 1786 vs 1769 sh, 1754 vs	KBr	[47]
PEt_3	1996 vs, 1879 w, 1848 m, 1808 vs 1780 s, 1769 s	Cyclohexane	[47]
PEt_3	1989 vs, 1879 w, 1844 s, 1798 vs 1776 vs, 1765 vs	THF	[47]
PEt_3	1984 vs, 1881 w, 1859 m-s, 1786 m, 1769 sh, 1751 vs	LP	[47]
PEt_3	1988 vs, 1878 w, 1842 m, 1797 vs 1778, 1778 vs, 1762 vs	Hexane	[48]
$P(C_6H_4\text{-}p\text{-}CH_3)_3$	1999 s, 1892 w, 1860 m, 1818 s, 1793 s,	$(C_2H_5)_2O$	[48]
$P(C_6H_4\text{-}p\text{-}OCH_3)_3$	1955 s, 1892 s, 1855 m, 1812 s, 1787 s	THF	[48]
PPh_2Et	1998 s, 1890 w, 1853 m, 1812 s, 1794 sh, 1784 s	$(C_2H_5)_2O$	[48]
PBu_3	1988 s, 1878 w, 1842 m, 1797 s, 1778 s, 1762 s	THF	[48]

*Solvate with three benzene molecules.

The structure of two solvates $Pt_5(CO)_6(PPh_3)_4.3Solv$ with toluene[47] and benzene[48] has been investigated. The structure of the pentanuclear cluster (Fig.5) can be regarded either as a tetrahedron with a Pt(1) metal bridge or as two orthogonal triangles with a common Pt(2) vertex;[47] the latter view is based on the presence in the molecule of the longer Pt(3)–Pt(5) and Pt(4)–Pt(5) bonds.

It is noteworthy that both X-ray diffraction data and the parameters of the infrared spectra of the pentanuclear cluster $Pt_5(CO)_6(PPh_3)_4$, obtained in two independent studies,[47,48] agree well. The infrared spectrum contains a set of bands in the ν(CO) region, characteristic of all the compounds obtained hitherto (Table 9). This agreement is not only between the number of bands but also between the ratios of their intensities. A pronounced dependence of the position and form of the low-frequency band (~1790 cm^{-1}) on the nature of the solvent (as far as the splitting of the band into two components) has also been noted.[36]

The highly characteristic nature of the infrared spectra of the pentanuclear clusters makes it possible to assume, in our view, that the compounds obtained previously,[22] to which the composition $Pt_4(CO)_5L_4$ (L = $AsPh_3$, PPh_2Bz, or PEt_3) was attributed, are apparently in reality clusters having the composition $Pt_5(CO)_6L_4$ or contain the latter in large amounts. This conclusion can be based on the analysis of the infrared spectra in the ν(CO) region. Bender and Braunstein[49] arrived at an analogous conclusion on the basis of the identity of the infrared spectra of $Pt_5(CO)_6(PEt_3)_4$ and the product to which the composition $Pt_4(CO)_5(PEt_3)_4$ had been attributed previously.[22] The compound $Pt_4(CO)_5(PPh_3)_3.1.5C_6H_6$ obtained by Ugo et al.[34] has a set of ν(CO) bands characteristic of pentanuclear clusters, but their positions differ appreciably from those of the ν(CO) bands for the compounds investigated. Thus in individual instances the form of the spectrum in the ν(CO) region is sufficiently characteristic to assign the clusters to a particular type.

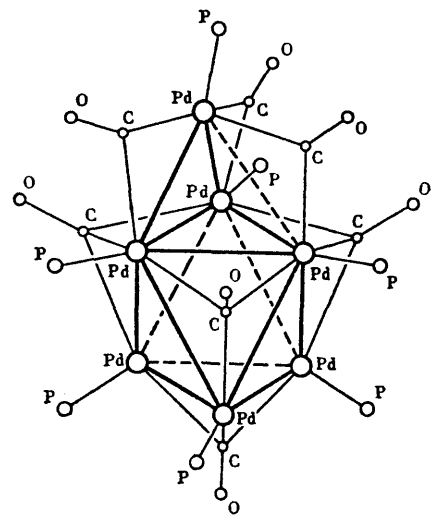


Figure 6. The structure of the $Pd_7(CO)_7(PMe_3)_3$ cluster.[51]

5. The Heptanuclear $Pd_7(\mu_3\text{-}CO)_4(\mu\text{-}CO)_3(PMe_3)_7$ Cluster

The heptanuclear cluster $Pd_7(CO)_7(PMe_3)_7$ has been obtained by reducing $Pd(\eta^1,\eta^3\text{-}C_8H_{12})(PMe_3)$ with carbon monoxide and is the only example of a cluster having the degree of nuclearity indicated.[51] Its structure has been established by X-ray diffraction (Fig.6). The cluster is a one-cap octahedron; the additional palladium atom is located asymmetrically over a face of the octahedron; one of the Pd_{cap}–Pd_{oct} distances is 3.18 Å, which greatly exceeds the lengths of the other two bonds (2.73 Å). The bond lengths within the octahedron are in the range 2.75–2.81 Å. The infrared spectrum of a specimen of the test substance

pelleted with KBr has absorption bands due to the CO groups in the low-frequency region (1825 s, 1800 v.s, 1785 sh, 1770 s, 1850 s, 1685 s).

6. The Decanuclear $Pd_{10}(CO)_{12}L_6$ and $Pd_{10}(CO)_{14}L_4$ Clusters

(a) Clusters with straight-chain aliphatic phosphines. The conditions of the synthesis of clusters of this type have been investigated in greatest detail. The compounds are formed when palladium acetate is reduced in the presence of trifluoroacetic acid. The special advantage of this method of synthesis is the possibility of obtaining individual compounds $Pd_{10}(CO)_{12}L_6$ (I) and (II) and $Pd_{10}(CO)_{14}(PBu_3)_4$ (V) within wide limits of the Pd : P ratios (Table 10).[41,52,53]

Table 10. The synthesis of the decanuclear palladium clusters by the reduction of $Pd(OAc)_2$.

Cluster		Pd:P *	Conditions of synthesis	Refs.
$Pd_{10}(CO)_{12}(PEt_3)_6$	(I)	1:3.3—1:15	Acetone, CF_3COOH	[52, 53, 46]
$Pd_{10}(CO)_{12}(PBu_3)_6$	(II)	1:4—1:10	Acetone, CF_3COOH	[52, 46]
$Pd_{10}(CO)_{14}(PEt_3)_4$ **	(III)	1:1.5—1:1.5	Acetone, CF_3COOH	[41, 27]
$Pd_{10}(CO)_{14}(PPr_3)_4$	(IV)	1:2	Acetone, CF_3COOH	[27]
$Pd_{10}(CO)_{14}(PBu_3)_4$	(V)	1:1.5—1:2.5	Acetone, CF_3COOH	[54]
$Pd_{10}(CO)_{12}[P(n\text{-}C_8H_{17})_3]_6$	(VI)	1:0.6	Acetone	[41]
$Pd_{10}(CO)_{12}[P(n\text{-}C_{12}H_{25})_3]_6$	(VII)	1:0.6	Acetone	[41]
$Pd_{10}(CO)_{12}(PPh_3)_6$	(VIII)	1:1—1:0.6	Acetone, NaOAc, HOAc	[29]
$Pd_{10}(CO)_{12}[P(C_6H_4\text{-}p\text{-}Me)_3]_6$	(IX)	1:0.7	Acetone, NaOAc, HOAc	[29]
$Pd_{10}(CO)_{12}[P(C_6H_4\text{-}p\text{-}OMe)_3]_6$	(X)	1:0.7	Acetone, NaOAc, HOAc	[29]

*The Pd : P molar ratio in the synthesis is quoted.
**In a mixture with compound (I).

Table 11. Infrared spectroscopic data for the decanuclear palladium clusters $Pd_{10}(CO)_{12}L_6$.

Ligand	ν(CO), cm^{-1}	Conditions	Refs.
PEt_3	2052 vw, 1921 sh, 1889 s, 1875 sh, 1850 s, 1841 sh, 1822 sh, 1806 sh, 1791 m or * 1892 s, 1853 s, 1790 m	LP	[27]
PEt_3	1892 s, 1875 m, 1856 s	Benzene	[27]
PBu_3	2038 vw, 1921 sh, 1889 s, 1878 sh, 1864 sh, 1852 s, 1827 sh, 1800 m or * 1884 s, 1850 s, 1799 m	LP	[27]
PBu_3 **	2034 s, 1914 s, 1898 s, 1871 s, 1818 s	LP	[27, 54]
$P(n\text{-}C_8H_{17})_3$	2032 w-m, 1920 sh, 1891 s, 1876 sh, 1856 s, 1800 m	Hexane film	[41]
$P(n\text{-}C_{12}H_{25})_3$	2034 w, 2017 vw, 1895 s, 1882 sh, 1859 s, 1835 sh, 1805 w	Hexane film	[41]
PPh_3	2036 w, 1906 s, 1893 m, 1870 s, 1839 shb, 1803 m	LP	[29]
PPh_3	1911 s, 1894 m, 1877 s, 1845 w-m, 1816 m	THF	[29]
$P(C_6H_4\text{-}p\text{-}Me)_3$	2023 w, 1906 s, 1893 m, 1872 s, 1847 s, 1809 m	LP	[29]
$P(C_6H_4\text{-}p\text{-}Me)_3$	1910 s, 1891 m, 1875 s, 1845 sh, 1815 m	THF	[29]
$P(C_6H_4\text{-}p\text{-}OMe)_3$	2036 w, 1901 s, 1889 m, 1867 s, 1832 sh 1803 m	LP	[29]
$P(C_6H_4\text{-}p\text{-}OMe)_3$	1906 s, 1890 m, 1872 s, 1845 sh, 1812 m	THF	[29]

*Depends on the degree of dispersion of the specimen in liquid paraffin.
**The $Pd_{10}(CO)_{14}(PBu_3)_4$ cluster.

The infrared and ^{31}P NMR spectra of the clusters (I), (II), and (V) have been obtained.[41,46,52–54] The absorption bands in the range 1810–1920 cm^{-1} which have been assigned to the vibrations of the bridging CO groups, and the bands at 2030–2040 cm^{-1}, assigned to the terminal CO groups, are characteristic of the infrared spectrum of cluster (V) (Table 11). The spectra of clusters (I) and (II) have a similar form and similar relative intensities of the ν(CO) bands. The spectra of clusters (II) and (V) are characterised by very similar sets of absorption bands of the bridging CO groups, but in the infrared spectrum of compound (V) these bands have undergone a hypsochromic shift of approximately 20 cm^{-1}.

The ^{31}P NMR spectrum of compound (V) (in benzene as the solvent) consists of a singlet with $\delta = -5.0$ p.p.m. The ^{31}P NMR spectra of clusters (III) and (I) are characterised by two signals with a 2 : 1 intensity ratio and $\delta = -4.0$ and +3.3 p.p.m. for compound (II) and $\delta = -11.0$ and −3.1 p.p.m. for compound (I).[52,53]

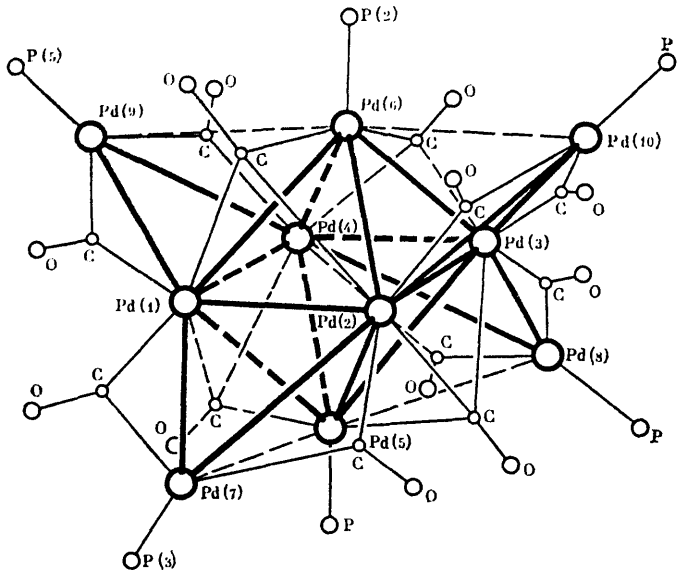


Figure 7. The structure of the $Pd_{10}(CO)_{12}(PBu_3)_6$ cluster.[53]

The spectroscopic data agree well with the structures of clusters (V) [54] and (II).[53] The structure of cluster (II) is illustrated in Fig. 7 (the n-butyl substituents are not shown).[53] Cluster (II) is an octahedron with capping palladium atoms located over its non-adjacent faces: the equatorial Pd(1)–Pd(4) atoms and the apical Pd(5) and Pd(6) atoms of the "internal" Pd_6 octahedron, as well as the Pd(7)–Pd(10) capping atoms. The Pd_{cap}–Pd_{eq} distances [2.694–2.722 (a) Å] are much smaller than the Pd_{cap}–Pd_{apic} distances [3.301–3.42 (2) Å]. The Pd–Pd distances in the internal "Pd_6" octahedral are in the range [2.791–2.851 (2) Å].[53] The eight μ_2-CO groups span the short Pd_{cap}–Pd_{eq} bonds and the four μ-CO groups are coordinated to the four free faces of the octahedron. The coordination of the CO groups to the faces is also asymmetric but, in contrast to the capping metal atoms, the carbon atoms of the μ_3-CO groups are displaced towards the apical palladium atoms, so that the Pd_{apic}–C distances [2.04–2.08 (2) Å] are shorter than the Pd_{eq}–C distances [2.23–2.35 (2) Å]. The six phosphorus

atoms of the tributyl phosphine ligands are linked to the four capping palladium atoms and the two apical palladium atoms. The ^{31}P NMR spectrum of these atoms is characterised by signals with $\delta = -4.0$ and +3.3 p.p.m.

Cluster (V) retains the same framework of metal atoms as cluster (II), but CO groups and not the PBu_3 ligand have been added to the apical palladium atoms. The $Pd_{cap}-Pd_{apic}$ distances in cluster (V) are shorter by approximately 0.015 Å than the analogous distances in cluster (II).[54] This shortening is apparently caused by the partial elimination of steric strain when the PBu_3 groups are replaced by CO groups. Another feature of the structure of cluster (V) is the presence in one molecule of three types of CO groups: four bridging μ_3-CO groups, eight bridging μ-CO groups, and two terminal groups.

(b) The influence of the acidity of the medium on the composition of the clusters. The replacement of trifluoroacetic acid by the weak acetic acid in the synthesis of the clusters $Pd_{10}(CO)_{12+x}L_{6-x}$ ($x = 0.2$) leads to a continuous variation of the composition of the product as a function of the Pd : P ratio. Under these conditions, the individual compounds (V) and (II) were obtained for stoichiometric Pd : P ratios; as the ratio decreases to 1 : 2.2, the $Pd_4(CO)_5 \cdot (PBu_3)_4$ cluster is formed. An analogous relation has been observed using PEt_3 as the ligand. It has been shown by spectroscopic methods that in the region of intermediate Pd : P ratios (from 1 : 06 to 1 : 2) a mixture of the $Pd_4(CO)_5 \cdot (PBu_3)_4$ and (II) clusters is formed.[41] In the case of triethylphosphine the mixture of compounds was resolved into the individual Pd_3 and Pd_7 clusters.[41]

Clusters having the compositions (VI) and (VII) have been obtained in a neutral medium for the stoichiometric Pd : P ratios and have been identified from infrared and ^{31}P NMR spectra. Their infrared spectra (Table 11) are analogous to those of the structurally characterised cluster (II). The ^{31}P NMR spectra of clusters (VI) and (VII) each containg two singlets with intensities in a ratio of 2 : 1, which corresponds to signals from phosphorus atoms coordinated to the four "capping" and two apical palladium atoms.[4]

It is noteworthy that in a neutral medium and in the HOAc + NaOc system with the Pd : PBu_3 = 1 : 0.4 ratio, cluster (II) with an admixture of metallic palladium is formed instead of the expected compound (V).[41] An important factor is the intermediate formation of the $Pd_4(CO)_5(PBu_3)_4$ cluster detected from the infrared spectra of the products in the initial stages of the reaction (in the HOAc + NaOAc system).[27,41]

On passing to a weakly alkaline medium (NaOAc) with the ratios Pd : PBu_3 = 1 : 1–1 : 1.4, $Pd_4(CO)_5(PBu_3)_4$ is formed in a mixture with metallic palladium, while under conditions with the ratio Pd : PBu_3 = 1 : 0.6, a mixture incorporating compound (II), $Pd_4(CO)_5(PBu_3)_4$ and metallic palladium is formed.[41]

The role of the acid consists of creating a specific equilibrium concentration of the free phosphine which is optimal for the formation of the cluster having the appropriate structure. Superstoichiometric amounts of $P(n\text{-}Alk)_3$ in the synthesis of compounds (I), (II), and (V) require the presence of a strong acid.[41,46,53] The excess ligand is bound in this case into the phosphonium salt $[HPAlk_3]^+ \cdot [CF_3COO]^-$. Otherwise in weakly acid and neutral media it is essential to reduce the concentration of $P(n\text{-}Alk)_3$ to give the stoichiometric ratios.[41]

A significant factor is that under the conditions of synthesis investigated and when the above trialkylphosphines are used, the "intermediate" $Pd_5-Pd_6-\ldots\ldots Pd_9$ structures cannot be detected either in solution or in the solid phase. Thus crystallisation during the synthesis in the $Pd(OAc)_2$–dioxan–Me_2CO–HX–PBu_3–H_2O–CO system leads only to clusters (II), (V), $Pd_4(CO)_5(PBu_3)_4$, and $Pd_4(CO)_6(PBu_3)_4$, depending on the Pd : PBu_3 ratio and the type of group X (X = CF_3COO^- or CH_3COO^-).[27,41]

(c) Clusters with aromatic phosphines. The lower basicity of aromatic phosphines precludes the regulation of their concentration by varying the acidity of the medium. The composition of the product is extremely sensitive to the Pd : P ratio during the synthesis and to the reaction time. The synthesis is therefore carried out under rigorously controlled conditions and yet despite this a reprecipitation is usually required to obtain a purer substance. Clusters (VIII)–(X) have been identified by elemental analysis and infrared spectroscopy (Table 11).[29]

7. Comparison of the Methods of Synthesis

Examination of the principal methods of synthesis of palladium and platinum clusters makes it possible to differentiate a number of common features. A low-valence complex of the metal, namely PdL_2, PtL_2, $Pt(cod)_2$, and $[Pt_3(CO)_6]_n^{2-}$, synthesised beforehand or obtained by reducing platinum(II) and palladium(II) in solution, is usually employed as the starting compound. Derivatives of the zerovalent metal are then converted into carbonyl-containing mononuclear complexes by treatment with carbon monoxide:

$$PtL_2 + 2CO \rightleftarrows Pt(CO)_2L_2;$$
$$Pd(OAc)_2 + 2CO + 3L + H_2O \rightarrow Pd(CO)L_3 + CO_2 + 2HOAc;$$
$$K_2PtCl_4 + 2L + CO \xrightarrow[N_2H_4]{KOH} Pt(CO)_2L_2.$$

As a consequence of the pronounced ability of zerovalent palladium and platinum compounds to form metal–metal bonds, in the presence of a deficiency of phosphine ligands the mononuclear phosphine metal carbonyl species are combined into clusters of different nuclearity depending on the conditions; this is shown particularly for the trinuclear compounds:

$$5Pt(CO)_2L_2 \rightleftarrows Pt_3(CO)_3L_4 + 2PtL_3 + 7CO;$$
$$3Pd(CO)L_3 \rightleftarrows Pd_3(CO)_3L_4 + 5L.$$

Another picture is observed when palladium dicarbonyl is used. X-Ray diffraction showed[15] that the $[Pt_3(CO)_6]_n^{2-}$ species have polymeric structures made up of three-membered rings linked by elongated Pt–Pt bonds. In this case mononuclear species are not produced[36] and attack by the phosphine results in the immediate splitting off of a fragment made up of three platinum atoms:

$$[Pt_3(CO)_6]_n^{-2} + 4PPh_3 \rightarrow Pt_3(CO)_3(PPh_3)_4 + [Pt_3(CO)_6]_{n-1}^{-2} + 3CO.$$

Furthermore, interconversions of clusters of different nuclearity are a common feature. Thus in an atmosphere of carbon monoxide the clusters $Pt_3(CO)_3(PPh_3)_4$ gradually disproportionates into $Pt_4(CO)_5(PPh_3)_4$ and a mononuclear complex:[22]

$$2Pt_3(CO)_3(PPh_3)_4 \xrightarrow{3CO} Pt_4(CO)_5(PPh_3)_4 + 2Pt(CO)_2(PPh_3)_2.$$

This process is particularly rapid for aliphatic phosphines, which precludes the synthesis of the trinuclear cluster with PEt_3 by reaction with platinum dicarbonyl. On the other hand, the high reactivity of the platinum clusters with aliphatic phosphines helps in effecting a wide variety of rearrangements of the clusters and leads to the selective formation of $Pt_4(CO)_5(PEt_3)_4$ and $Pt_5(CO)_6(PEt_3)_4$. The yield

and nuclearity of the clusters are in this case determined solely by the Pt : L ratio:[30]

$$[Pt_3(CO)_6]_n^{2-} + PEt_3 \rightarrow Pt_4(CO)_5(PEt_3)_4 + CO;$$
$$[Pt_3(CO)_6]_{n2}^{-} + PEt_3 \rightarrow Pt_5(CO)_6(PEt_3)_4 + CO.$$

The process involving an increase of nuclearity can be made more selective and rapid by binding the phosphines. The removal of the phosphines from the reaction media (by treatment with H^+, O_2, etc.) makes it possible to obtain clusters of high nuclearity immediately from the mononuclear species. This process has been investigated for palladium compounds.[55,56] In the case of platinum, $Pt_5(CO)_6(PEt_3)_4$ has been obtained in a high yield from the complex $Pt_4(CO)_5.(PEt_3)_4$ on treatment with CF_3COOH:

$$5Pt_4(CO)_5(PEt_3)_4 + 4CF_3COOH \rightarrow 4Pt_5(CO)_6(PEt_3)_4 + 4[HPEt_3]^+CF_3COO^- + CO.$$

In the synthesis of the pentanuclear platinum clusters by the method of Bender and co-workers[47,49] involving the reduction of $PtCl_2L_2$ by carboxylate ions, the interconversion of the clusters probably also takes place. The method yields as a rule a mixture of compounds, the most stable form $Pt_5(CO)_6L_4$ being separated in the chromatographic stage. This has been confirmed by a later study[50] where impregnation of different carriers by the $Pt_3(CO)_3L_4$ clusters leads to their conversion into pentanuclear compounds $Pt_5(CO)_6L_4$.

Much less complex transformations take place in the synthesis of the pentanuclear platinum clusters in the reaction of phosphine ligands with $[Pt_3(CO)_6]_n^{2-}$. As already mentioned, in this case the first reaction stage involves the formation of $Pt_3(CO)_3L_4$ and this stage is rapid. The compound then reacts slowly with platinum dicarbonyl to form $Pt_5(CO)_6L_4$:[36]

$$Pt_3(CO)_3L_4 + [Pt_3(CO)_6]_n^{2-} \rightarrow Pt_5(CO)_6L_4 + CO.$$

In the case of aliphatic phosphines the rates of both stages are similar and the trinuclear cluster is therefore obtained always in a mixture with compounds with a higher nuclearity. It is noteworthy that the Pt_4 cluster in solution does not undergo disproportionation and its conversion into the Pt_5 cluster requires the elimination of the phosphine ligand and its chemical binding. The disproportionation reactions take place for all the palladium cluster compounds, including the decanuclear clusters.[55,56]

III. THE INTERCONVERSION OF PHOSPHINEPALLADIUM CARBONYL CLUSTERS

It was found that in the synthesis of phosphine metal carbonyl clusters the acidity of the medium has a strong influence on the formation of compounds with a particular nuclearity; this observation has been used to synthesise one compound from another. The above possibility has been realised experimentally in two studies,[55,56] which led to the development of the method for increasing the nuclearity of phosphinepalladium carbonyl compounds. The method is based on the binding of the phosphine-containing ligand. The choice of reactant depends on the basicity of the phosphine ligand and includes acids, oxidants, organohalogen compounds, and complexes of metals in different oxidation states:[27,55,56]

$$PR_3 + H^+ \text{ (or } {}^1/_2O_2) \rightarrow HPR_3^+ \text{ (or } OPR_3); \quad (1)$$
$$PR_3 + R'X \rightarrow [R'PR_3]^+X^-; \quad (2)$$
$$nPR_3 + M(CO)_x \rightarrow M(CO)_{x-n}(PR_3)_n + nCO; \quad (3)$$
$$2PR_3 + MX_2 \rightarrow (PR_3)_2MX_2. \quad (4)$$

1. The Interconversions of Clusters in the Pd(0)–CO–P(n-Alk)$_3$ System

In a system with tri-n-alkylphosphine ligands the clusters undergo interconversions with a change in the degree of their nuclearity and the composition of the coordination shell. The $Pd_4 \rightleftharpoons Pd_{10}$ interconversion is the key factor:[55]

$$5Pd_4(CO)_5[P(n\text{-Alk})_3]_4 + 8H^+ \rightarrow 2Pd_{10}(CO)_{12}[P(n\text{-Alk})_3]_6 + 8[HP(n\text{-Alk})_3]^+ + CO;$$
$$2Pd_{10}(CO)_{12}[P(n\text{-Alk})_3]_6 + 8P(n\text{-Alk})_3 + CO \rightarrow 5Pd_4(CO)_5[P(n\text{-Alk})_3]_4.$$

The interconversion takes place with a high selectivity (>90%). The transformation $Pd_4 \rightarrow Pd_{10}$ has been carried out by treating $Pd_4(CO)_5(PEt_3)_4$ with iron pentacarbonyl (88% of compound (I) was obtained] and by treating $Pd_4(CO)_5(PBu_3)_4$ with palladium acetate or 8-bromomethylquinoline, i.e. on the basis of reactions (2)–(4). A compound from the family of phosphine palladium carbonyl clusters can also be used as an acceptor of the phosphorus-containing ligand:[55]

$$10Pd_{10}(CO)_{14}(PBu_3)_4 + 11Pd_4(CO)_5(PBu_3)_4 \rightarrow 14Pd_{10}(CO)_{12}(PBu_3)_6 + 27CO + 4Pd.$$

Cluster (II) has also been obtained from the complex PdL_4, where L = PBu_3 but with a lower yield (10%):[55]

$$10\,PdL_4 + 34\,H^+ + 12\,CO \rightarrow Pd_{10}(CO)_{12}L_6 + 34\,HL^+.$$

The reactions, which take place with a change in the composition of the coordination shell, include the following processes:[46,55]

$$Pd_{10}(CO)_{12}(PBu_3)_6 + 2H^+ + 2CO \rightarrow Pd_{10}(CO)_{14}(PBu_3)_4 + 2HPBu_3;$$
$$Pd_{10}(CO)_{14}(PBu_3)_4 + 2PBu_3 \rightarrow Pd_{10}(CO)_{12}(PBu_3)_6 + 2CO;$$
$$Pd_4(CO)_5(PBu_3)_4 + CO \rightarrow Pd_4(CO)_6(PBu_3)_4. \quad (5)$$
(XI)

In order to obtain the pure compound (V) by reaction (5), it is necessary to monitor the latter with respect to time: on treatment with an excess of H^+, metallic palladium is gradually formed.[54,55]

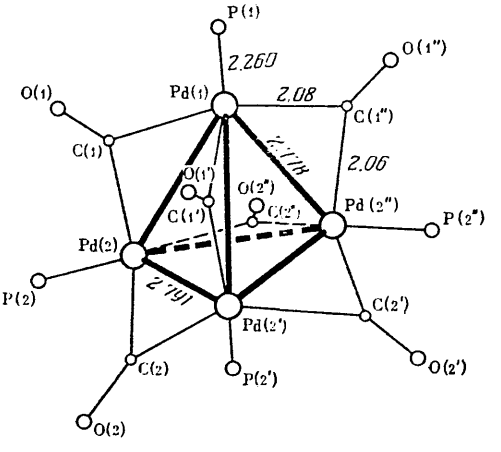


Figure 8. The structure of the $Pd_4(CO)_6(PBu_3)_4$ cluster.[46]

The structurally characterised cluster (XL) (Fig.8) has been obtained by crystallising $Pd_4(CO)_5(PBu_3)_4$ in a CO atmosphere.[46] The cluster consists of a virtually undistorted tetrahedron, all the edges of which are spanned by

the μ-CO ligands and each palladium atom is coordinated to one phosphorus atom of the phosphine ligand.

Thus the overall mechanism of the interconversion of the phosphinepalladium carbonyl clusters in the Pd(0)–CO–P(n-Alk)$_3$ system can be represented as follows:

$$PdL_4 \underset{L,N_2,\Delta}{\overset{CO}{\rightleftarrows}} Pd(CO)L_3 \underset{L}{\overset{CO,\,H^+}{\rightleftarrows}} Pd_4(CO)_5L_4 + Pd_4(CO)_6L_4 \underset{L}{\overset{CO,\,H^+}{\rightleftarrows}}$$
$$\rightleftarrows Pd_{10}(CO)_{12}L_6 \underset{L}{\overset{CO,\,H^+}{\rightleftarrows}} Pd_{10}(CO)_{14}L_4 \begin{cases} \xrightarrow{CO,\,H^+} Pd \\ \xrightarrow[L]{} PdL_4 \end{cases}.$$

This mechanism constitutes a clear illustration of one of the definitions of clusters as compounds intermediate between the classical mononuclear complexes and compact metal.

2. The Interactions of the Clusters in the Pd(0)–CO–PPh$_3$ System

The use of an acid to increase the nuclearity of clusters in this system is ineffective owing to the low basicity of the aromatic phosphine ligand. Up to $n = 4$, the binding of the triphenylphosphine ligand is not essential in view of the existence of the following equilibria in the solutions:[33,35,56–58]

$$PdL_4 + CO \rightleftarrows Pd(CO)L_3 + L;$$
$$3\,Pd(CO)L_3 \rightleftarrows Pd_3(CO)_3L_4 + 5\,L;$$
$$4\,Pd_3(CO)_3L_4 + 3\,CO \rightleftarrows 3\,Pd_4(CO)_5L_4 + 4\,L.$$

The $Pd_3(CO)_3(PPh_3)_4$ cluster is much more stable than its analogue with the PBu_3 ligand, which could not be isolated. In solution in a CO atmosphere the $Pd_3(CO)_3(PPh_3)_4$ cluster is converted into the tetranuclear $Pd_4(CO)_5(PPh_3)_4$ cluster previously characterised as $Pd_3(CO)_3L_3$.[35,58] We may note that the platinum cluster $Pt_3(CO)_3L_4$ disproportionates under similar conditions into $Pt_4(CO)_5L_4$ and $Pt(CO)_2L_2$.[22]

The composition and yield of the products of crystallisation of the compounds PdL_4, $Pd(CO)L_3$, and $Pd_3(CO)_3L_4$ in a CO atmosphere depend on the concentrations of the starting materials, the nature of the solvent, the reaction time, the temperature, and the composition of the gas phase. In some cases it is possible to obtain crystals containing two different clusters. Thus the joint crystallisation of two clusters, i.e. $Pd_3(CO)_3(PPh_3)_4Pd_4(CO)_5(PPh_3)_4.C_6H_6$, has been observed by X-ray diffraction.[33]

In solution in an atmosphere of CO the $Pd_4(CO)_6(PPh_3)_4$ cluster is also in equilibrium with the form having a higher nuclearity, namely the cluxter (VIII).[56]

The decanuclear cluster (VIII) has been obtained by oxidising PdL_4, $Pd(CO)L_3$, $Pd_3(CO)_3(PPh_3)_4$, or $Pd_4(CO)_5(PPh_3)_4$ with an oxygen–carbon monoxide mixture (in proportions of 2 : 1):[27,56]

$$10PdL_4 + 17O_2 + 12CO \rightarrow Pd_{10}(CO)_{12}L_6 + 34OL;$$
$$10Pd_4(CO)_5L_4 + 9O_2 \xrightarrow{CO} 4Pd_{10}(CO)_{12}L_6 + 16OL + 2CO_2. \qquad (6)$$

The formation of cluster (VIII) in these reactions has been demonstrated by elemental analysis, infrared spectroscopy (Table 11), and ^{31}P NMR of the solution at the end of the oxidation reaction.[27,56] The ^{31}P NMR spectrum of the solution in toluene[56] indicates the formation of $OPPh_3$ (–23.7 p.p.m.) and cluster (VIII), which gives rise to two signals, at –23.0 and –15.9 p.p.m., with an intensity ratio of approximately 2 : 1. The difference between their chemical shifts (7.1 p.p.m.) is the same as in the ^{31}P NMR spectra of clusters (I) and (II) (7–8 p.p.m.).[41,52,53] The relative signal intensities $OPPh_3 : PPh_3 = 1 : 1.6$ confirm the stoichiometry of reaction (6).

A decrease of nuclearity with formation of the individual compounds is achieved in the interaction with phosphine in the ratios (VIII) : L = 1 : 7), (VIII) : L = 1 : 11, and $Pd_4(CO)_5(PPh_3)_4$: L = 1 : 2.5 respectively:[56]

$$2Pd_{10}(CO)_{12}L_6 + 8L + CO \xrightarrow{\text{toluene}} 5Pd_4(CO)_5L_4;$$
$$3Pd_{10}(CO)_{12}L_6 + 22L \xrightarrow{\text{acetone}} 10Pd_3(CO)_3L_4 + 6CO;$$
$$3Pd_4(CO)_5L_4 + 4L \xrightarrow{\text{acetone}} 4Pd_3(CO)_3L_4 + 3CO.$$

Treatment of any of the clusters $Pd_3(CO)_3L_4$, $Pd_4(CO)_5L_4$, or (VIII) with an excess of the ligand L leads to the complex PdL_4.

The triphenylphosphinepalladium carbonyl clusters are also formed in the disproportionation reactions of clusters of different nuclearity.[56] The interaction of the stoichiometric amounts of Pd_3 and (VIII) in the presence of L in toluene leads to the Pd_4 cluster:

$$6\,Pd_3(CO)_3L_4 + Pd_{10}(CO)_{12}L_6 + 5\,CO \rightarrow 7\,Pd_4(CO)_5L_4 + 2\,L.$$

The $Pd_4(CO)_5L_4$ cluster has been obtained by the interaction of compound (VIII) and PdL_4 in toluene in the ratio (VIII) : PdL_4 = 1 : 2:

$$Pd_{10}(CO)_{12}L_6 + 2\,PdL_4 + 3\,CO \rightarrow 3\,Pd_4(CO)_5L_4 + 2\,L.$$

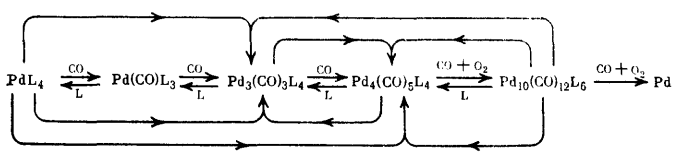
The highly labile $Pd_3(CO)_3L_4$ cluster is not formed in appreciable amounts in solution even under favourable stoichiometric conditions; the products of the reaction of compound (VIII) and PdL_4 in toluene for the ratio (VIII) : PdL_4 = 1 : 4 are $Pd_4(CO)_5(PPh_3)_4$ and $Pd(CO)L_3$:[56]

$$Pd_{10}(CO)_{12}L_6 + 4\,PdL_4 + 5\,CO \rightarrow 3\,Pd_4(CO)_5L_4 + 2\,Pd(CO)L_3 + 4\,L.$$

However, the interaction in acetone, in which all the compounds involved in the reaction are sparingly soluble, leads to the formation of $Pd_3(CO)_3L_4$ for the molar ratios (VIII) : : PdL_4 = 1 : 5 and $Pd_4(CO)_5L_4$: PdL_4 = 1 : 2:[56]

$$Pd_{10}(CO)_{12}L_6 + 5\,PdL_4 + 3\,CO \rightarrow 5\,Pd_3(CO)_3L_4 + 6\,L;$$
$$Pd_4(CO)_5L_4 + 2\,PdL_4 + CO \rightarrow 2\,Pd_3(CO)_3L_4 + 4\,L.$$

The overall mechanism of the interconversions of triphenylphosphinemetal carbonyl compounds can be formulated as follows:



An important property of the Pd(0)–CO–PR$_3$ system, where R = n-Alk and R = Ph, is the formation of isotypical Pd_4 and Pd_{10} clusters, although the PPh_3 group differs from P(n-Alk)$_3$ (for example, from PBu_3) in its steric and electronic characteristics.[59]

In contrast to the Pd(0)–CO–P(n-Bu)$_3$ system, in the system with the triphenylphosphine ligand it is not possible to isolate in a pure state the second decanuclear cluster $Pd_{10}(CO)_{14}L_4$. An increase of the duration of the treatment of solutions of the clusters $Pd_4(CO)_5(PPh_3)_4$ or (VIII) with the CO + O_2 mixture leads to the formation of a mixture of $Pd_{10}(CO)_{12}L_6$, $Pd_{10}(CO)_{14}L_4$, and metallic palladium.[56] Another difference consists of the existence of the trinuclear $Pd_3(CO)_3(PPh_3)_4$ cluster, which is stable in the solid state. As in the system with PBu_3, in that with PPh_3 it has not so far been possible to isolate compounds with an intermediate nuclearity in the range $4 < n \leq 9$.[56]

IV. CHEMICAL PROPERTIES

It is possible to differentiate two types of reactions characteristic of phosphinepalladium carbonyl clusters, namely the substitution and oxidative addition reactions. By virtue of the polynuclearity of the initial compounds, each of these reactions can lead in the general case to products of two types—with retention of the initial structure or with a change in nuclearity up to the formation of mononuclear compounds:[27]

$$Pd_n(CO)_x(PR_3)_y \begin{cases} \xrightarrow[\text{of ER}_3]{\text{substitution}} \begin{cases} \longrightarrow \text{«}Pd_n\text{»}; \\ \longrightarrow Pd(ER_3)_{3,4}; \end{cases} \\ \xrightarrow[\text{addition of RX, RHgX}]{\text{oxidative}} \begin{cases} \longrightarrow \text{«}Pd_n\text{»}; \\ \longrightarrow (PR_3)_2Pd(R)(X) + [(PR_3)Pd(RCO)X]_2 \text{ etc.}; \end{cases} \end{cases}$$

E = P, As, Sb; X = Cl, Br, I.

Cluster (V), being most depleted in the phosphine ligand, is suitable for substitution reactions. Depending on the ratio (V) : substituting ligand, compounds with different nuclearities n = 10, 4, or 1) and heterogeneous (for n = 10 or 4) or homogeneous (for n = 4 or 1) phosphorus-containing ligands are formed. Thus treatment of compound (V) with a solution PPh_3 as L in the proportions (V) : L = 1 : 2 yielded the $Pd_{10}(CO)_{12}(PBu_3)_4(PPh_3)_2$ cluster:

$$Pd_{10}(CO)_{14}(PBu_3)_4 + 2\ PPh_3 \rightarrow Pd_{10}(CO)_{12}(PBu_3)_4(PPh_3)_2 + 2\ CO,$$

while reaction involving the proportions 1 : 3.7 yielded the $Pd_{10}(CO)_{12}(PBu_3)(PPh_3)_5$ cluster.[27]

It has been shown that the triphenylphosphine ligand in the compound $Pd_{10}(CO)_{12}(PBu_3)_4(PPh_3)_2$ is coordinated not only to the apical palladium atoms but also to the capping palladium atom in the proportions $L_{cap} : L_{apic} = 1.8 : 1.0$.[27] A ^{31}P NMR study showed that the observed coordination of triphenylphosphine is caused by the simultaneous substitution of the terminal CO groups at the apical palladium atom and of the PBu_3 groups at the capping atom (with some predominance of the substitution of the CO groups). The PBu_3 liberated in this process can also substitute terminal CO groups.[27]

The decomposition of the structures of the $Pd_{10}(CO)_{14}\cdot(PBu_3)_4$ and $Pd_{10}(CO)_{12}(PBu_3)_6$ clusters with formation of $Pd_4(CO)_5(PBu_3)_{4-n}(PPh_3)_n$ clusters has been observed in the presence of a more than 4-molar excess of PPh_3. A further increase of the amount of PPh_3 (up to $Pd_{10} : PPh_3$ = 1 : 12) leads to the formation of a mixture of $Pd(CO)(PPh_3)_3$ and $Pd(PPh_3)_4$.[27] Treatment of the compound $Pd_4(CO)_5\cdot(PBu_3)_4$ with triphenylphosphine in the proportions $Pd_4 : PPh_3$ = 1 : 2 gives rise to a mixture of $Pd_4(CO)_5\cdot(PBu_3)_{4-n}(PPh_3)_n$ (where $n \cong 2$–4), $Pd(CO)(PPh_3)_3$, and $Pd(PPh_3)_4$.[27]

The interaction of the Pd_{10} clusters with an excess of L = ER_3, where E = P, As, or Sb, in the proportions $Pd_{10} : ER_3$ = 1 : 40 and less leads to the mononuclear PdL_4 complexes and can be regarded as yet another method of synthesis of these compounds:[27]

$$Pd_{10}(CO)_{12}(PAlk_3)_6 + 40\ ER_3 \rightarrow 10\ Pd(ER_3)_4 + 12\ CO + 6\ PAlk_3.$$

The complexes $Pd(PR_3)_x$ have been obtained for R—OPh (x = 4) and R = p-$CH_3C_6H_4$ or p-$CH_3OC_6H_4$ (x = 3).[27]

The advantage of the proposed method[27] of synthesis of PdL_4 and similar complexes over the familiar method[60] lies in the presence in the coordination shell of the initial cluster of carbon monoxide as the dominant ligand, which can be readily removed into the gas phase and does not therefore prevent the isolation of the pure substance.

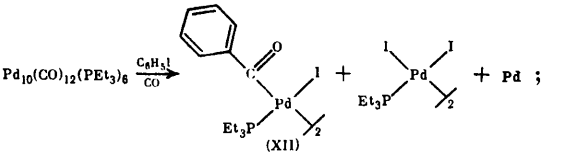
The majority of the oxidative addition reactions have been carried out with trialkylphosphinemetal carbonyl clusters Pd_4 and Pd_{10}.[61] Almost all the reactions are accompanied by the elimination of CO and the decomposition of the initial structure.

The reactions with RX and RHgX yielded products both containing the carbonyl group in the R—CO—Pd fragment and without it, as in R—Pd; carbonyl-containing compounds are then formed regardless of whether the reaction is carried out in an atmosphere of CO or in an inert gas. Furthermore, metallic palladium is produced and the compounds $[PdI_2\cdot(PEt_3)]_2$, $PdBr_2(PBu_3)_2$, etc. are formed. A wide variety of products can be accounted for, apart from the possibility of different reaction pathways, by the chemical non-equivalence of the Pd atoms in the Pd_{10} cluster. As mentioned above, three types of palladium atoms can be differentiated in the Pd_{10} structure (Fig. 7)—equatorial, capping, and apical. Among these the capping and apical atoms are most accessible to the attacking molecule, while the equatorial atoms, which lack phosphine ligands, are primarily responsible for the formation of metallic palladium. The interaction of RX, RHgX, or R_2Hg with one of the outer Pd atoms apparently causes a rapid decomposition of the $Pd_{10}(Pd_4)$ structure. The ratio of the oxidative addition products and the metal is then determined solely by the relative rates of reaction of the decomposing Pd_{10} (or Pd_4) fragments with RX, RHgX, or R_2Hg and their agglomeration to the metal.[61]

In the reaction with an excess of C_3H_5Cl the metal is not produced as a consequence of the formation of the compound $[(\eta^3\text{-}C_3H_5)Pd]_2$, which does not require additional phosphine ligands:[27]

$$Pd_{10}(CO)_{12}(PBu_3)_6 + 10\ C_3H_5Cl \rightarrow 2[(\eta^3\text{-}C_3H_5)PdCl]_2 + 6(\eta^3\text{-}C_3H_5)PdCl(PBu_3) + 12\ CO.$$

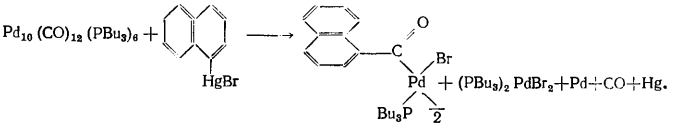
The reaction of iodobenzene with compound (I) in an atmosphere of CO and the reaction of bromobenzene with $Pd_4(CO)_5\cdot(PEt_3)_4$ in an atmosphere of N_2 lead to di-μ-iodobis[benzoyl(triethylphosphine)palladium] (XII), phenylbis(triethylphosphine)palladium bromide (XIII), and benzoylbis(triethylphosphine)palladium bromide (XIV):[27]



$$Pd_4(CO)_5(PEt_3)_4 + C_6H_5Br \xrightarrow{N_2} \underset{\text{(XIII)}}{(Ph)(Br)Pd(PEt_3)_2} + (PhCO)(Br)Pd(PEt_3)_2 + Br_2Pd(PEt_3)_2 + Pd + CO.$$

(XIV)

The interaction of α-naphthylmercury bromide with cluster (II) takes place with liberation of mercury in accordance with the general mechanism of redox demercuration[62] and is accompanied by the insertion of the CO group and the formation of di-μ-bromobis[α-naphthoyltributylphosphinepalladium]:[61]

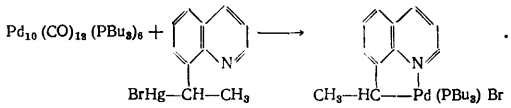


A mononuclear diarylpalladium derivative has been obtained by reaction (7) in the light in the course of seven days:[61]

$$Pd_{10}(CO)_{12}(PBu_3)_6 + (C_6F_5)_2Hg + Ph_2PC_2H_4PPh_2 \rightarrow (C_6F_5)_2Pd(Ph_2PC_2H_4PPh_2). \quad (7)$$

A chelate σ-complex of palladium(II) has been obtained as

one of the products of the reaction with 8-(α-bromomercuriethyl)quinoline:[61]



A second product of the same reaction proved to be a cluster whose infrared spectrum contains two bands due to the bridging CO groups at 1900 and 1860 cm^{-1} and which could not be isolated. However, its triethylphosphine analogue has been obtained by the reaction of the cluster $Pd_4(CO)_5(PEt_3)_4$ with 8-(α-bromomercuriethyl)quinoline.

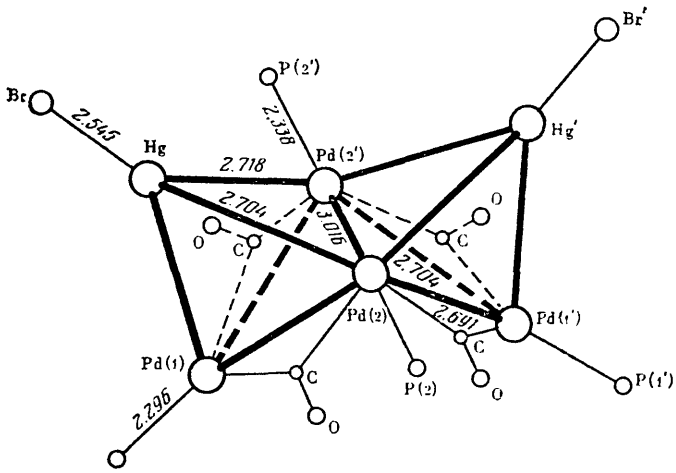


Figure 9. The structure of the $Pd_4Hg_2(CO)_4(PEt_3)_4Br_2$ cluster.[63]

The elemental composition and structure of the first heteronuclear palladium-mercury cluster $Pd_4Hg_2(CO)_4(PEt_3)_4 \cdot Br_2$ has been established by X-ray diffraction (Fig.9).[63] The cluster consists of a "butterfly", both "wings" of which are centred on the Hg—Br fragments. All the Pd—Pd bonds, with the exception of the elongated "hinged" bonds, are spanned by the μ_2-CO groups, each palladium atom being coordinated to a phosphorus atom. One may assume[27] that the charges in the cluster are separated up to the attainment of the limiting state $[(Pd_4(CO)_4(PEt_3)_4]^{2-}[HgBr]_2^{2+}$, In this compound both the anion and cation should be fairly stable: the anion is isoelectronic with the stable $Pd_4(CO)_5(PEt_3)_4$ cluster, while the mercury in the cation is in its usual +2 oxidation state.

The second heteronuclear palladium-mercury cluster has been obtained by the reaction of $Pd_4(CO)_5(PEt_3)_4$ with mercury:[64]

$$2\ Pd_4(CO)_5(PEt_3)_4 + Hg \rightarrow Pd_6Hg(CO)_6(PEt_3)_6 + 4\ CO + 2\ PEt_3 + 2\ Pd.$$

The formula of the compound has been proposed on the basis of analytical data and a cryoscopic determination of the molecular weight. In the suggested structure (Fig.10) all the CO groups are bridging (the bands at 1862 and 1822 cm^{-1} in the infrared spectrum) and span all six Pd—Pd bonds. Each palladium atom is coordinated to one phosphorus atom of the phosphine ligand.

The information available about reactions involving oxidative addition to triphenylphosphinepalladium(0) carbonyl clusters is limited: only the complex [Pd(I).(PhCO)(PPh_3). .toluene] (apparently with a dinuclear structure) has been obtained by treating a solution of PhI and $Pd_3(CO)_3(PPh_3)_4$ in toluene with carbon monoxide; $Pd(PhCO)(I)(PPh_3)_2$ was obtained as an admixture.[65]

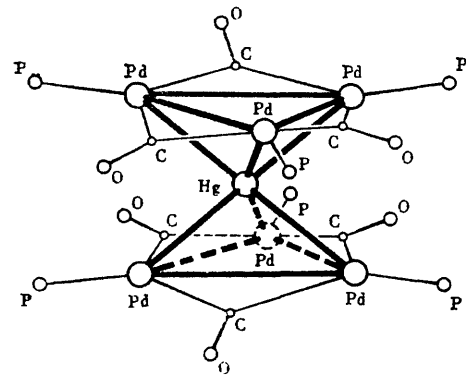


Figure 10. The suggested structure of the $Pd_6Hg(CO)_6 \cdot (PEt_3)_6$ cluster.[64]

The $Pd_3(CO)_3(PPh_3)_4$ [35] and $Pd_4(CO)_5(PPh_3)_4$ [33,35] clusters catalyse the methoxycarbonylation of aryl halides under mild conditions,[65] but the compounds themselves apparently decompose during the reaction. The following mechanism of the process has been proposed:[65-67]

$$PdL_n + PhI \rightarrow (Ph)Pd(I)L_{n-2} + 2\ L;$$
$$(Ph)Pd(I)L_{n-2} + CO \rightarrow (PhCO)Pd(I)L_{n-2};$$
$$(PhCO)Pd(I)L_{n-2} + CH_3OH \rightarrow PhCOOCH_3 + (H)Pd(I)L_{n-2};$$
$$(H)Pd(I)L_{n-2} + 2\ L + R_2NH \rightarrow PdL_n + R_2NH_2^+ + I^-.$$

where L is carbon monoxide, phosphine, or a solvent molecule. The activities of the substrates vary inversely to the C—halogen bond energy: PhI > PhBr ≫ PhCl.

The chemical properties of phosphineplatinum(0) carbonyl clusters have so far been inadequately investigated; we shall examine the main ones.

The interaction of the trinuclear clusters with carbon monoxide leads to tetranuclear platinum clusters. In contrast to the corresponding reaction of the $Pd_3(CO)_3L_4$ palladium cluster, a second platinum-containing product is formed in this reaction, namely a mononuclear complex:[22]

$$Pt_3(CO)_3L_4 + CO \rightarrow Pt_4(CO)_5L_4 + Pt(CO)_2L_2.$$

The removal of the phosphine ligands in the form of quaternary phosphonium salts or complexes with other metals is accompanied by a rearrangement of the skeleton:[48,50]

$$Pt_3(CO)_3(PPh_3)_4 \xrightarrow[\text{sorbent}]{H^+} Pt_5(CO)_6(PPh_3)_4;$$
$$Pt_4(CO)_5(PEt_3)_4 \xrightarrow[Fe(CO)_5]{H^+} Pt_5(CO)_6(PEt_3)_4.$$

Treatment with a measured amount of the phosphine ligand leads either to a cluster with a smaller number of platinum atoms in the metallic skeleton [32] or to the complete decomposition of the skeleton to mononuclear zerovalent platinum compounds: [22]

$$Pt_4(CO)_5(PEt_3)_4 + PEt_3 \xrightarrow{N_2} Pt_2(CO)_3(PEt_3)_4 + Pt(PEt_3)_x;$$
$$Pt_3(CO)_3(PPh_3)_4 + dppe \rightarrow Pt(dppe)_2 + CO + PPh_3;$$
$$dppe = Ph_2PC_2H_4PPh_2.$$

The latter reaction is used for the volumetric determination of the CO content in the cluster. [22]

The reaction of phosphineplatinum carbonyl clusters with SO_2 yielded the corresponding SO_2 containing clusters (with retention of the skeleton): [8]

$$Pt_3(CO)_3(PPh_3)_4 + 3\ SO_2 \rightarrow Pt_3(SO_2)_3(PPh_3)_3 + CO + PPh_3;$$
$$Pt_4(CO)_5(PMe_2Ph)_4 + 5\ SO_2 \rightarrow Pt_4(SO_2)_5(PMe_2Ph)_4 + 5\ CO;$$
$$Pt_3(CO)_6(PPh_3)_4 + 3\ SO_2 \rightarrow Pt_3(CO)_2(SO_2)_3(PPh_3)_4 + 4\ CO.$$

In the last case the SO_2 groups substitute all the CO groups with the exception of the terminal and one of the basal groups in the tetrahedral fragment. The reverse process, i.e. the displacement of the SO_2 groups by carbon monoxide, takes place with rearrangement of the skeleton: [8]

$$Pt_3(SO_2)_3(PPh_3)_3 \xrightarrow[CO]{60^\circ C} Pt_3(CO)_6(PPh_3)_4 + SO_2.$$

Oxidation of the trinuclear $Pt_3(CO)_3[P(t\text{-}Bu)_3]_3$ cluster with a stoichiometric amount of iodine leads to a dinuclear platinum(I) complex: [68]

$$Pt_3(CO)_3[P(t\text{-}Bu)_3]_3 + I_2 \rightarrow [PtI(CO)P(t\text{-}Bu)_3]_2.$$

The reaction with mercury takes place in a somewhat unusual manner. The trinuclear $Pt_3(CO)_3L_3$ clusters, where L = PPh(iso-Pr)$_2$, P(iso-Pr)$_3$, or PEt(t-Bu), react with mercury to form compounds in which two triangles made up of platinum atoms are linked by an Hg–Hg chain. [69] The reaction with $Pt_4(CO)_5(PEt_3)_4$ leads to the $Hg[Pt_3(CO)_3 \cdot (PEt_3)_3]_2$, which has a sandwich structure where the mercury atom links symmetrically two planar triangles made up of platinum atoms. [69]

Analysis of the literature data has shown that phosphine-metal carbonyl clusters are most typical for palladium and platinum. Whereas compounds with n = 3, 4, or 5 are known for platinum, compounds with n = 3, 4, 7, or 10 are known for palladium. Reactions involving a change in nuclearity are characteristic of palladium and platinum clusters.

The great possibilities of clusters in the formation of effective catalysts must be emphasised. The creation of effective catalytic systems based on cluster compounds will probably constitute in the immediate future the theoretically and practically most important trend in the development of catalysis.

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Cluster Transition Metal Chalcogenide Halides

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The literature data on cluster transition metal chalcogenide halides are described systematically and discussed. The structures of these compounds are examined and compared with those of the analogous cluster metal halides and chalcogenides. The principal preparative methods of synthesis of the cluster chalcogenide halides are discussed and a systematic account is given of the first results obtained in the study of the chemical properties of this class of inorganic compounds.
The bibliography includes 102 references.

CONTENTS

I. Introduction 408
II. The structure of cluster metal chalcogenide halides 408
III. Methods of synthesis 419
IV. Chemical properties 421

I. INTRODUCTION

The principal advances achieved in the chemistry of cluster compounds in recent years are associated primarily with the synthesis and the determination of the structures of numerous low-valence carbonyl clusters of different nuclearity, especially those characteristic of Group VIII metals.[1-4] The formation of metal carbonyl clusters is much less characteristic of the elements at the beginning of the transition series; cluster compounds with "classical" acido-ligands such as halogens and chalcogens have long been known for these metals and have been thoroughly investigated.[5-8] In contrast to the low-valence metal carbonyl clusters, in the cluster compounds with "classical" ligands the metal atom has a higher formal oxidation state and these compounds are therefore classified as high-valence clusters.[4] Although the first representative of transition metal halide clusters was obtained as early as the beginning of the century,[9] vigorous studies on the cluster niobium, tantalum, molybdenum, tungsten, and rhenium halides as well as their complexes with various ligands have been carried out in the last two decades.[5,6,8] The first structural study of cluster compounds was performed in relation to the hexanuclear molybdenum cluster.[10] The structures of the complexes of metals at the beginning of the transition series with halide ligands, in which the number of metal atoms in the cluster group varies from two to six, have now been investigated.

The chemistry of transition metal chalcogenides, in which the metal–metal pair interactions take place or clusters containing three, four, six, nine, and more metal atoms are formed is also being vigorously studied.[7] The interest in compounds of this kind has increased particularly after the discovery of superconductivity in the so called Chevrel phases which are cluster formations.[11]

A polymeric type of structure, in which bridging ligands link the cluster nuclei into infinite chains, layers, or three-dimensional formations are characteristic of cluster transition metal halides and chalcogenides. An extremely interesting feature of certain cluster halides and chalcogenides is the ability of the metallic clusters to link up with one another to produce the so-called condensed clusters.[7] For example, in the structures of binary and ternary phases of the lower transition metal halides and chalcogenides it is possible to differentiate infinite chains consisting of M_6 octahedra linked to one another via common vertices, edges, or faces.[7]

An important class of inorganic compounds consists of transition metal chalcogenide halides in which the metal atoms are coordinated simultaneously to halogens X and chalcogens Y. The chalcogenide halides have long been known,[12] but the most important results in their investigation have been obtained in the last decade.[13-15]

The main efforts of investigators have been directed to the search for reactions leading to the formation of new chalcogenide halides, the optimisation of the conditions of synthesis, and the determination of their structure, while inadequate attention has been devoted to the chemical properties of the chalcogenide halides.

Fig.1 presents the known cluster transition metal chalcogenide halides, i.e. the chalcogenide halides in which the existence of metal–metal bonds has been established on the basis of structural and other data. Evidently the formation of cluster chalcogenide halides is characteristic of metals at the beginning of the transition series, i.e. of metals for which cluster halides and chalcogenides are known.

This review discusses the structure, syntheses, and chemical properties of dinuclear, trinuclear, tetranuclear, and hexanuclear cluster transition metal chalcogenide halides.

II. THE STRUCTURE OF CLUSTER METAL CHALCOGENIDE HALIDES

1. Dinuclear Chalcogenide Halides

(a) The Chalcogenide Halides $NbYX_3$ (Y = Se or Te; X = Cl, Br, or I)

All the niobium chalcogenide halides having the general formula $NbYX_3$ are isostructural and crystallise in the monoclinic system (space group $P/2a$, $Z = 2$).[16] The unit cell parameters of the compounds $NbYX_3$ are presented in Table 1.

The structures of $NbSeBr_3$, $NbTeBr_3$, and $NbTeI_3$ have been determined.[16] The crystal-chemical formula is $[Nb_2(\mu_2\text{-}Y_2)(\mu_2\text{-}X)_2X_2(\mu_2\text{-}X)_{4/2}]_\infty$. The formal oxidation state of the metal is +4. The principal structural motif is illustrated in Fig.2*a*. It is made up of two niobium atoms with Nb = Nb distances of 2.832, 2.875, and 2.932 Å respectively for $NbSeBr_3$, $NbTeBr_3$, and $NbTeI_3$. The dichalcogenide group Y_2 is coordinated asymmetrically to two niobium atoms in relation to the metal–metal bond (rotation of the Y_2 dumbell by 4–5° from the "orthogonal" position towards the metal–metal bond). The distances in the chalcogenide group Y_2, which are 2.305 Å for Se–Se and 2.670–2.685 Å for Te–Te, are close to the length of a single bond (2.34 Å for Se_2 and 2.76 Å for Te_2).[17]

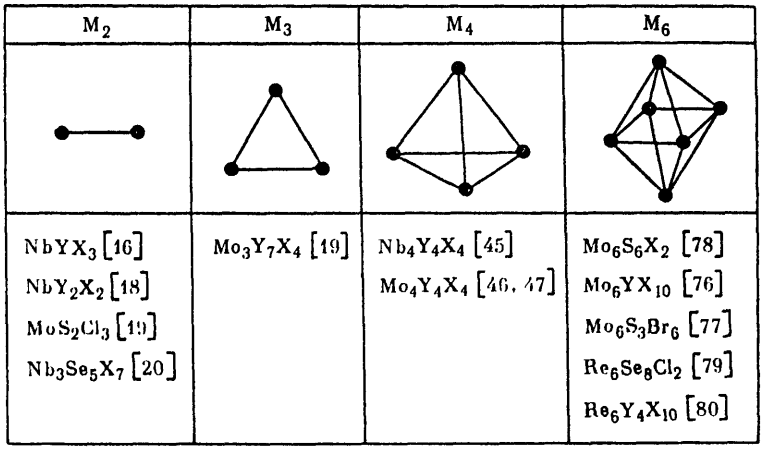


Figure 1. Types of cluster transition metal chalcogenide halides [the numbers in square brackets denote references (Translator)].

Table 1. The unit cell parameters of the cluster chalcogenide halides.

Compound	Unit cell parameters						Density, g cm^{-3}		Refs.
	a, Å	*b*, Å	*c*, Å	α°	β°	γ°	d_{exp}	d_{calc}	
$NbSeCl_3$	11.913	6.714	6.347	—	98.83 (1)	—	—	—	[16]
$NbSeBr_3$	12.540 (12)	6.897 (10)	6.624 (10)	—	98.9 (1)	—	—	4.830	[16]
$NbTeBr_3$	12.597 (13)	7.135 (9)	6.670 (9)	—	97.6 (1)	—	—	5.144	[16]
$NbTeI_3$	13.473 (3)	7.429 (2)	7.141 (2)	—	98.52 (2)	—	—	5.649	[16]
NbS_2Br_2*	6.528 (2)	6.589 (2)	7.254 (1)	67.72 (2)	112.63 (2)	120.05	—	—	[18]
NbS_2I_2*	6.77	6.80	7.23	73.80	102.30	117.4	4.49	4.53	[18]
$NbSe_2Cl_2$*	6.350 (2)	6.538 (3)	7.261 (2)	66.93 (3)	111.35 (3)	119.01 (3)	4.48	4.51	[18]
$NbSe_2Br_2$*	6.667 (2)	6.724 (2)	7.084 (2)	79.40 (2)	111.83 (2)	119.68 (1)	—	—	[18]
$NbSe_2I_2$*	7.060 (1)	7.207 (2)	7.757 (2)	67.59 (2)	113.20 (3)	121.10 (2)	5.48	5.54	[18]
NbS_2Cl_2**	6.27	11.09	6.69	—	111.07	—	3.47	3.49	[18]
NbS_2Br_2**	6.54	11.32	6.91	—	110.54	—	4.30	4.34	[18]
$NbSe_2Cl_2$**	6.64	11.23	6.96	—	108.93	—	—	—	[18]
$NbSe_2Br_2$**	6.76	11.53	7.20	—	113.90	—	5.28	5.32	[18]
$NbSeI_2$**	6.89	12.34—12.46	7.51	—	112.26	—	—	—	[18]
MoS_2Cl_3	6.186	7.244	13.345	—	116.17	—	3.32	3.31	[19]
$Nb_3Se_5Cl_7$	7.599	12.675	8.051	—	106.27	—	4.04	4.110	[20]
$Nb_3Se_5Br_7$	7.621	12.833	8.069	—	106.21	—	—	—	[20]
$Mo_3S_7Cl_4$	9.336	12.185	13.956	—	122.90	—	3.23	3.26	[19]
$Nb_4S_4Br_4$	10.193	—	—	—	—	—	—	—	[45]
$Nb_4S_4I_4$	10.639	—	—	—	—	—	—	—	[45]
$Nb_4Se_4Br_4$	10.368	—	—	—	—	—	—	—	[45]
$Nb_4Se_4I_4$	10.782 (3)	—	—	—	—	—	—	6.332	[45]
$Mo_4S_4Cl_4$	9.68	—	—	—	—	—	—	—	[46, 47]
$Mo_4S_4Br_4$	9.94 (5)	—	—	—	—	—	5.55	5.61	[46, 47]
$Mo_4S_4I_4$	10.33	—	—	—	—	—	—	—	[46, 47]
Mo_6SCl_{10}	9.811 (7)	13.768 (7)	11.821 (9)	—	—	—	3.94	4.00	[76]
Mo_6SeCl_{10}	9.899 (8)	13.783 (11)	11.834 (11)	—	—	—	4.12	4.15	[76]
Mo_6TeCl_{10}	10.078 (9)	13.855 (9)	11.837 (12)	—	—	—	4.20	4.25	[76]
Mo_6SBr_{10}	10.23	14.35	12.24	—	—	—	5.17	5.20	[76]
Mo_6SeBr_{10}	10.28	14.35	12.29	—	—	—	5.26	5.33	[76]
Mo_6TeBr_{10}	10.44	14.35	12.35	—	—	—	5.30	5.39	[76]
Mo_6SeI_{10}	10.86	15.24	13.18	—	—	—	5.84	5.86	[76]
Mo_6TeI_{10}	11.00	15.24	13.20	—	—	—	5.85	5.92	[76]
$Mo_6S_3Br_6$	17.250 (7)	6.600 (4)	11.929 (7)	—	—	—	5.51	5.63	[77]
$Mo_6S_6Br_2$	9.545 (4)	—	10.357 (3)	—	—	—	5.60	5.66	[78]
$Mo_6S_6I_2$	9.639	—	10.437	—	—	—	5.80	6.06	[78]
$Re_6Se_8Cl_2$	6.598	6.640	9.071	100.19	113.52	83.14	—	8.52	[79]
$Re_6Se_4Cl_{10}$	8.898 (5)	8.957 (5)	12.627 (10)	84.20 (4)	84.60 (4)	82.19 (3)	6.05	6.10	[80]

*Low-temperature modification.
**High-temperature modification.

Two bridging halogen atoms (μ_2-X) are coordinated analogously and they too are located asymmetrically in relation to the Nb–Nb bond. This asymmetry can be accounted for by the van der Waals repulsion of the halogen atoms. Each niobium atom is linked to one terminal halogen atom X; the length of the bond between niobium and the terminal halogen atom is somewhat smaller than the distance between niobium and the bridging halogen atom. The niobium–niobium fragments are linked by the bridging hydrogen atoms into an infinite chain structure.

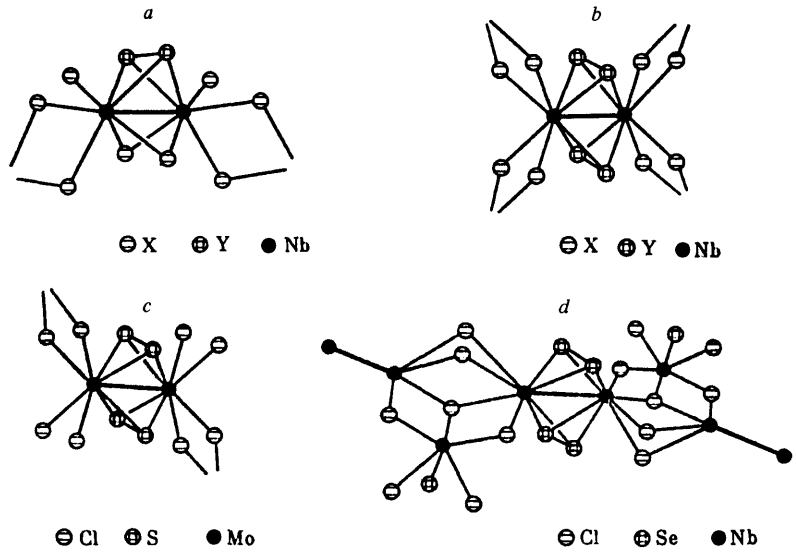


Figure 2. The structure of dinuclear niobium and molybdenum chalcogenide halides: *a*) $NbYX_3$;[16] *b*) NbY_2X_2;[18] *c*) MoS_2Cl_3;[19] *d*) $Nb_3Se_5Cl_7$.[20]

(b) The Chalcogenide Halides NbY_2X_2 (Y = S or Se; X = Cl, Br, or I)

The chalcogenide halides NbY_2X_2 crystallise in the triclinic system under normal conditions (space group $P\bar{1}$, $Z = 2$).[18] The compound NbS_2Cl_2, which has a monoclinic cell at room temperature, is an exception (Table 1). On heating, most of these phases undergo polymorphic transformations (except NbS_2I_2, which does not exhibit polymorphism); there is then a transition from a triclinic to a monoclinic unit cell (space group $C2/m$, $Z = 4$).[18] Table 1 lists the unit cell parameters for the low-temperature and high-temperature modifications of these phases.

The structure of the niobium chalcogenide halides having this composition has been established in relation to the triclinic modification of $NbSe_2Cl_2$ and the monoclinic form of NbS_2Cl_2.[18] The principal structural motif of the given dinuclear complex is presented in Fig. 2*b*. Two niobium atoms are located at the vertices of a distorted Nb_2Y_4 octahedron (D_{2h} symmetry), in which the dichalcogenide groups Y_2, coordinated to the niobium atoms as bridging ligands, make up the equatorial plane. The Nb–Nb distances in these fragments are respectively 2.871 Å in NbS_2Cl_2 and 2.873 Å in $NbSe_2Cl_2$. An interesting crystal-chemical feature of this fragment is the extremely short Y–Y distances in the Y_2 groups, amounting to 1.996 Å for S–S and 2.272 Å for Se–Se. The coplanarity of the S–S bonds in NbS_2Cl_2 indicates the absence of asymmetry in the position of Y_2, noted above in connection with the $NbYX_3$ phases. Admittedly, a slight asymmetry of the orientation of the Se–Se bonds is retained in $NbSe_2Cl_2$. The octahedral Nb_2Y_4 fragments are linked by bridging halogen atoms into layers, i.e. this structure has a layer character.

Thus the crystal-chemical formula of compounds of this type can be represented as follows:

$$[Nb_2(\mu\text{-}Y_2)_2(\mu_2\text{-}X)_{8/2}]_\infty .$$

The formal oxidation state of niobium in such compounds is +4.

(c) The Molybdenum Sulphide Chloride MoS_2Cl_3

The molybdenum sulphide chloride MoS_2Cl_3 crystallises in the monoclinic system (space group $P2_1/c$, $Z = 4$).[19] The unit cell parameters are listed in Table 1.

The MoS_2Cl_3 structure (Fig. 2*c*) can be easily obtained from the NbS_2Cl_2 structure (Fig. 2*b*) by replacing the four bridging chlorine atoms in the *trans*-positions in NbS_2Cl_2 by the terminal atoms. We shall not discuss in detail the structure of MoS_2Cl_3, which is in many respect analogous to NbS_2Cl_2; the Mo–Mo distance is 2.833 Å. In contrast to NbS_2Cl_2, the polymeric motifs in the MoS_2Cl_3 crystals are combined in space in a different manner, namely via the bridging chlorine atoms in the *trans*-positions, which leads to a three-dimensional structure. The oxidation state of molybdenum in this compound is +5.

Among the other crystal-chemical characteristic features of the MoS_2Cl_3 structure, we may mention that the distance between molybdenum and the terminal chlorine atom (2.39 to 2.45 Å) is significantly shorter than the distance between molybdenum and the bridging chlorine atom (2.51–2.56 Å). The short S–S distances (1.98 Å) in the disulphide group S_2 and the absence of asymmetry in their coordination to the two molybdenum atoms are notable.

(d) The Niobium Chalcogenide Halides $Nb_3Se_5X_7$ (X = Cl or Br)

The niobium selenide chloride $Nb_3Se_5Cl_7$ and the niobium selenide bromide $Nb_3Se_5Br_7$ crystallise in the monoclinic system (space group $P2_1/m$, $Z = 2$);[20] the unit cell parameters are presented in Table 1.

A structure of this type has been investigated in relation to $Nb_3Se_5Cl_7$. It can be regarded as derived from the MoS_2Cl_3 structure as a result of the replacement in the latter of each pair of terminal chlorine atoms in the *trans*-positions by the two unusual ligands $NbSeCl_3$ (Fig. 2*d*). The $NbSeCl_3$ ligand

is coordinated to two niobium atoms belonging to neighbouring dinuclear fragments. We may note the short distances between the niobium atom in the $NbSeCl_5$ ligand and the niobium atoms in the neighbouring dinuclear fragments (3.15 Å). Two chlorine atoms in the $NbSeCl_5$ ligand are of the μ_2-bridging type [the Nb–(μ_2-Cl) distances are 2.582 and 2.553 Å], while the third chlorine atom is of the μ_3-bridging type (the distances from μ_3-Cl to the three nearest niobium atoms are 2.629, 2.629, and 2.727 Å). This type of binding of the dinuclear fragment leads to the formation of a chain structure.

The shortest Nb–Nb distance in $Nb_3Se_5Cl_7$ is 2.944 Å. The diselenide groups Se_2 in the central Nb_2Se_4 motif exhibit an appreciable asymmetry in relation to the Nb–Nb bond.

(e) The Nature of the Metal–Metal Chemical Bond in the Dinuclear Chalcogenide Halides

In conclusion of the discussion of the structures of the dinuclear niobium and molybdenum chalcogenide halides, we may mention yet again the common crystal-chemical features of these phases:

1. The dichalcogenide ligands Y_2 (Y = S, Se, or Te), coordinated to both metal atoms, are located in the central dinuclear fragment in all the compounds. The cross-linking of the fragments into chains (for $NbYX_3$ and $Nb_3Se_5Cl_7$) and planar or three-dimensional networks (for NbY_2X_2 and MoS_2Cl_3) is achieved via the bridging halogen atoms.
2. The short metal–metal bonds (2.8–2.9 Å) within the dinuclear fragment alternate with relatively long metal–metal distances (3.9–4.3 Å) between these fragments.

As a result of the efforts of a number of teams of Soviet and foreign specialists, considerable progress has now been achieved in understanding the nature of the metal–metal bond in the dinuclear and polynuclear molecular cluster compounds.[6,21–26] Many properties of the molecular dinuclear compounds can be reasonably explained on the basis of simple theoretical models widely employed at the present time.[5,6,26,27] On the other hand, in the case of polymeric cluster transition metal chalcogenide halides, in the interpretation of the properties of which it is essential to take into account a weaker extended interaction, theoretical models developed in detail are not so far available.

The formation of metal–metal bonds in dinuclear niobium and molybdenum chalcogenide halides can be described qualitatively in approximate terms on the assumption that the metal–ligand bonds are ionic. This approach is widely used in discussing M–M bonds in dinuclear complexes of acido-ligands and has made it possible to account for many properties of these compounds (in particular, magnetic properties). Indeed, bearing in mind the oxidation states of molybdenum and niobium (Mo^{5+} and Nb^{4+}) which obtain in the dinuclear chalcogenide halides as well as the diamagnetism of these compounds, one may conclude that metal–metal bonds are formed. Here one can assume that the valence electrons of the niobium and molybdenum atoms used to form the M–M bonds populate the highest molecular orbital of the σ-type which is largely made up of the *d* orbitals of the metal atoms. This result is in qualitative agreement with the calculation of the molecular orbital diagram for the $[Nb_2(Se_2)_2]^{4+}$ cluster fragment,[28] according to which the highest occupied molecular orbital is of the σ-type, consisting to the extent of 90% of the *d* orbitals of the niobium atom.

The evaluation of the number of valence electrons of the metal atoms in accordance with Sidgwick's rule, the applicability of which to dinuclear molecular complexes has been discussed,[29] may serve as an additional basis for the assumption that the metal–metal bond does or does not exist. According to this rule, the M–M bond is absent if the number of valence electrons in the two metal atoms is 36. The evaluation of the number of valence electrons for the known dinuclear chalcogenide halides with metal–metal bonds shows that the number corresponding to the two metal atoms in the central fragment is less than 36.

The character of the M–M bond can change significantly after the appearance of intracluster bridging ligands of different types (halide and chalcogenide) and also on formation of polymer chains or two-dimensional networks from the dinuclear fragments as a result of their cross-linking by bridging intercluster halide ligands. In the former case the character of the metal–metal bond (in particular, its length) is determined to a large extent by the electronic and geometrical characteristics of the intracluster bridging ligands, while in the second there is a possibility of additional delocalisation of electron density between metal atoms belonging to different dinuclear fragments. In the general case the estimation of each factor separately is a complex experimental and theoretical problem whose solution is simplified when a series of related compounds are considered.[30]

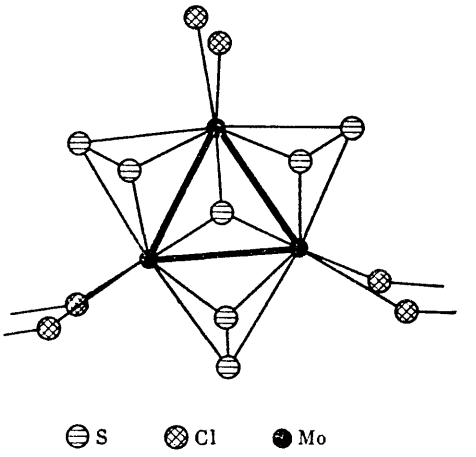


Figure 3. The structure of the trinuclear molybdenum sulphide chloride $Mo_3S_7Cl_4$.[19]

2. The Trinuclear Molybdenum Chalcogenide Halides $Mo_3Y_7X_4$ (Y = S or Se; X = Cl, Br, or I)

Of the six representatives of the trinuclear molybdenum chalcogenide halides $Mo_3Y_7X_4$, a structural study has been carried out for only one phase—the sulphide chloride $Mo_3S_7Cl_4$ (Fig. 3). The compound crystallises in the monoclinic system (space group $P2_1/c$, $Z = 4$;[19] its unit cell parameters are listed in Table 1). The three molybdenum atoms form a virtually equilateral triangle (the Mo–Mo distances are 2.748, 2.741, and 2.747 Å). One sulphur atom (μ_3-S) is located above the centre of the triangle and is linked to the three molybdenum atoms of the cluster. Two chlorine atoms in the molecule are terminal and belong to one molybdenum atom. Two pairs of chlorine atoms at the other two molybdenum atoms function as bridges linking the clusters into an

infinite zig-zag chain. The crystal-chemical formula of the trinuclear molybdenum sulphide chloride can be written thus:

The formal oxidation state of the metal in the trinuclear clusters $Mo_3Y_7X_4$ is +4.

The molybdenum chalcogenide halides $Mo_3S_7Br_4$, $Mo_3Se_7Cl_4$, $Mo_3Se_7Br_4$, $Mo_3S_7I_4$, and $Mo_3Se_7I_4$ were obtained by the same methods as $Mo_3S_7Cl_4$.[89-92] The identical compositions, the common methods of synthesis, and the consistent variation of the thermal properties and infrared spectra in the series of these compounds suggest that their structures are similar.

Within the framework of the ion-covalent model, it is assumed that the three molybdenum atoms in the cluster chalcogenide halide $Mo_3S(S_2)_3.Cl_2Cl_{4/2}$ provide 12 electrons for the formation of bonds with the ligands. Six electrons then remain for the binding of the metal atoms in the triangular Mo_3 cluster and the formal order of the Mo–Mo bond is 1.

On the other hand, evaluation of the number of valence electrons on the assumption of the formation of single Mo–Mo bonds shows that each molybdenum atom then achieves the electronic configuration of the nearest inert gas. This simplest treatment is in good agreement with experimental data: the Mo–Mo distances in the Mo_3 triangle are close to the metal–metal distance in metallic molybdenum.[17]

Speaking of the M–M distances in cluster systems of this kind, one should note in the first place the significant role of the geometrical and electronic properties of the intracluster bridging ligands.[31] To illustrate this, Table 2 presents the Mo–Mo distances in a series of trinuclear molybdenum clusters (structural type—triangle with a single cap). Table 2 shows that in compounds with a μ_3-bridging sulphur atom the Mo–Mo distances are much greater in compounds where oxygen is the μ_3-bridging atom.

Table 2. The metal–metal distances in the trinuclear cluster molybdenum compounds.

Compound	R (Mo–Mo), Å	N_0^*	Refs.
$Mo_3S(S_2)_3Cl_{4/2}Cl_2$	2.75	6	[19]
$[Mo_3S(S_2)_6]^{2-}$	2.72	6	[32]
$[Mo_3S_4(CN)_9]^{5-}$	2.77	6	[33]
$[Mo_3S_4Cp_3]^+$	2.81	6	[34]
$[Mo_3O_4F_9]^{5-}$	2.50	6	[35]
$Zn_2Mo_3O_8$	2.52	6	[36]
$[Mo_3O_4(acac)_3(EtO)_3]$	2.47	6	[37]
$[Mo_3O_4(C_2O_4)_3(H_2O)_3]^{2-}$	2.49	6	[38]
$[Mo_3OCl_3(Oac)_3(H_2O)_3]^{2+}$	2.55	8	[39]

*The number of skeletal electrons per Mo_3 cluster.

The most typical intracluster bridging ligands in the dinuclear and polynuclear chalcogenide halides are the dichalcogenide groups $(Y_2)^{2-}$ which in many respects determine the structure of the central motifs. Such groups can be readily identified by spectroscopic methods. For example, the stretching vibrations of the Y–Y bond are manifested in the Raman spectra by a highly intense band.[40,41] Analysis of the kinematic factors established that, for a fairly large difference between the masses of the metal and sulphur atoms, the hypsochromic shift of the $\nu_{(S-S)}$ frequency, due to the kinematic interaction of the S–S and M–S vibrations, is insignificant (~1 cm^{-1}).

The Raman spectra of numerous compounds containing the disulphide fragment S_2 have been investigated and the linear relations between the $\nu_{(S-S)}$ vibration frequency and the S–S bond length has been noted.[40,41] This made it possible to estimate the S–S bond length in the compounds $Mo_3S_7Br_4$ and $Mo_3S_7I_4$. Table 3 lists the S–S bond lengths in the S_2 dichalcogenide fragment obtained from X-ray diffraction data and calculated from Raman spectra.

Table 3. Dependence of the vibration frequency in the Raman spectra on the S–S bond length in the disulphide fragment.[40,100]

Compound	$\nu_{(S-S)}$, cm^{-1}	R (S–S), Å	
		from X-ray diffraction data	from Raman spectroscopic data
NbS_2Cl_2	592	1.996	1.99
$Mo_3S_7Cl_4$	570	2.01	2.01
$Mo_3S_7Br_4$	567	—	2.01
$Mo_3S_7I_4$	554	—	2.02
$[Mo_3S(S_2)_6]^{2-}$	545	2.02	2.03
$[Mo_2(S_2)_6]^{2-}$	530	2.043	2.04
$Mo_2(S_2)(S_2C_2Ph_2)_4$	518	2.04	2.05

3. The Tetranuclear Chalcogenide Halides $M_4Y_4X_4$ (M = Nb or Mo; Y = S or Se; X = Cl, Br, or I)

The tetranuclear cluster chalcogenide halides $M_4Y_4X_4$ have been obtained for niobium and molybdenum.[45-47] All the compounds crystallise in the cubic system (space group $F\bar{4}3/m$; the unit cell parameters are listed in Table 1).

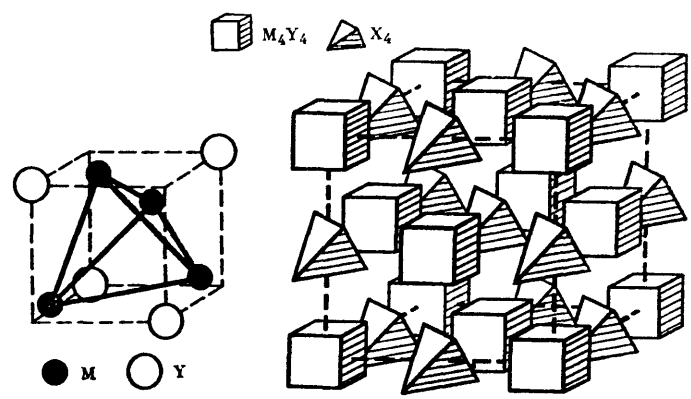


Figure 4. The structure of the tetranuclear niobium and molybdenum chalcogenide halides: *a*) the M_4Y_4 cluster group; *b*) three-dimensional representation of $M_4Y_4X_4$ made up of the M_4Y_4 cluster groups and the X_4 tetrahedra (M = Nb or Mo; Y = S or Se).[45-47]

Their structures have been investigated in relation to niobium selenide iodide $Nb_4Se_4I_4$ and molybdenum sulphide bromide $Mo_4S_4Br_4$. The structure of $Nb_4Se_4I_4$ was determined by the powder method[45] and that of $Mo_4S_4Br_4$ by X-ray diffraction of single crystals.[46,47]

(a) The Structure of $Nb_4Se_4I_4$

Niobium selenide iodide is a tetranuclear cluster containing the Nb_4Se_4 cluster group formed by interpenetrating Nb_4 and Se_4 tetrahedra (Fig. 4*a*).[45] The Nb_4Se_4 groups and the I_4 tetrahedra alternate in the $Nb_4Se_4I_4$ cubic lattice like the sodium and chlorine atoms in the NaCl crystal lattice (Fig. 4*b*). The Nb–Nb distance is 2.96 Å, which appreciably exceeds the Nb–Nb distance in metallic niobium (2.86 Å).[48] Each niobium atom is surrounded by three halogen atoms (the Nb–I distance is 3.02 Å), by three chalcogen atoms (the Nb–Se distance is 2.57 Å), and by three niobium atoms.

(b) The Structure of $Mo_4S_4Br_4$

The compound $Mo_4S_4Br_4$ has the same structure as $Nb_4Se_4I_4$.[46,47] The molybdenum and sulphur atoms occupy the vertices of the Mo_4S_4 pseudocube, the molybdenum atoms being somewhat displaced from its vertices to its centre, so that an Mo_4 tetrahedral cluster is produced. The Mo–Mo distance in the cluster (2.80 Å) is comparable to the metal–metal distance in metallic molybdenum (2.79 Å).[48] The Mo–Br (2.73 Å) and Mo–S (2.34 Å) distances in the octahedral environment of molybdenum are close to those observed in molybdenum bromides and sulphides.[55]

Another approach to the description of the structures of the niobium and molybdenum compounds $M_4Y_4X_4$ is also possible. The structure of these compounds can be represented as of the quasi-spinel type in which the anionic sublattice is made up of X and Y atoms (Fig. 4*b*). The metal atoms occupy half of the octahedral cavities usual for the chalcogenide spinels, are displaced towards the centre of the M_4Y_4 cube, and form the M_4 cluster.

A structure of the quasi-spinel type is known for ternary chalcogenides, for example, $GaMo_4S_8$, $AlMo_4S_8$,[49] and $MMo_2Re_2S_8$.[50] The framework in all these compounds consists of the M_4Y_4 tetrahedral cluster.

In the binary transition metal halides and chalcogenides tetrahedral clusters have not been so far observed, while the "butterfly" and "planar butterfly" structures obtain respectively in the anionic tetranuclear halides $[Mo_4I_{11}]^{2-}$ [51] and $[Nb_4Cl_{11}]^{2-}$.[52]

The niobium and molybdenum chalcogenide halides $M_4Y_4X_4$ are diamagnetic. Assuming an ionic model, one can postulate that the metal atoms give up 12 electrons for the formation of bonds with the ligands Y and X. In the molybdenum compounds the remaining 12 electrons in the Mo_4 cluster are used to form Mo–Mo bonds (two electrons for each edge of the tetrahedron). The formal order of the metal–metal bond in the Mo_4 tetrahedron is 1. In the niobium compound only eight electrons remain for the formation of metal–metal bonds and four electron pairs can participate in the formation of three-centre bonds along the edges of the Nb_4 tetrahedron.

4. The Hexanuclear Cluster Chalcogenide Halides

Ternary compounds of molybdenum and rhenium of the following composition belong to the hexanuclear chalcogenide halides: $Mo_6Y_{8-x}X_x$ (Y = Se, Te; X = Br, I); $Mo_6S_6X_2$ (X = Br, I); Mo_6YX_{10} (Y = S, Se, Te; X = Cl, Br, I); $Mo_6S_3Br_6$; $Re_6Se_8Cl_2$; $Re_6Y_4X_{10}$ (Y = Se, Te; X = Cl, Br). In the hexanuclear chalcogenide halides the metallic clusters constitute as a rule M_6 octahedra distorted to some extent.

For a deeper understanding of the crystal-chemical features and the somewhat unusual stoichiometry of the hexanuclear metal chalcogenide halides, it is useful to compare these phases with, on the one hand, the halide complexes and, on the other, the chalcogenide systems in which similar cluster fragments are produced.

We shall consider briefly the structures of the octahedral clusters of the above three types.

(a) Octahedral Clusters in Halide Systems

In the crystal chemistry of the lower molybdenum and tungsten halides (binary and ternary phases), the cluster group $[M_6X_8]$, which consists of six metal atoms forming the M_6 octahedron and eight halogen atoms located at the vertices of the X_8 cube (Fig. 5*a*), is well known. The M_6 octahedron is inscribed into the X_8 cube in such a way that the X atoms are located above the triangular faces of the octahedron, i.e. behave as μ_3-ligands.

In the halide systems of refractory metals the cluster groups carry a positive charge, namely $[M_6X_8]^{n+}$.[5] Each metal atom in such a group is capable of coordinating one additional ligand with formation of fragments of the type $[M_6X_8]L_6$, where L can be the same atom as X or a ligand of another kind (Fig. 5*b*). Such fragments are the main structural motif in virtually all compounds containing the $[M_6X_8]$ cluster group. Numerous binary and complex molybdenum(II) and tungsten(II) halides as well as the lower niobium iodide Nb_6I_{11} and its derivatives belong to this class of compounds.[5,53–55]

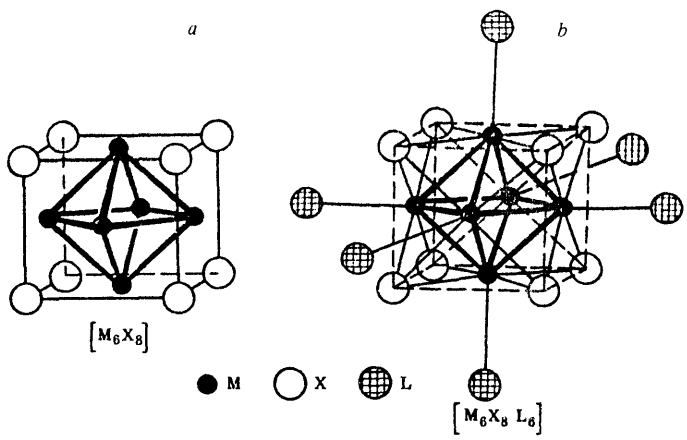


Figure 5. The cluster structure of the octahedral halide complexes: *a*) the $[M_6X_8]$ cluster group; *b*) the $[M_6X_8]L_6$ octahedral complex.

The complexes $[M_6X_8]L_6$ can be formed not only from the given molecules "own" atoms, which is observed in complexes of the type $M'_n[M_6X_8]L_6$, but also in compounds where the total number of ligands per M_6 cluster is less than 14. In these cases the coordination takes place via ligands belonging to other fragments, i.e. the ligands L become μ_2-bridging and belong simultaneously to two neighbouring cluster groups (intercluster bridges). Structures with two bridges, i.e. $[M_6X_8]L_4L_{2/2}$, four bridges, i.e. $[M_6X_8]L_2L_{4/2}$, or six bridges, i.e. $[M_6X_8]L_{6/2}$, are known. For example, certain lower niobium and molybdenum halides can be represented by the following crystal-chemical formulae: $[Nb_6I_8]I_{6/2}$;[56]

$[Mo_6Cl_8]Cl_2Cl_{4/2}$;[57] $[Mo_6Br_8]Br_4.2H_2O$.[58] The formula $[Nb_6I_8]I_{6/2}$ means that all the cluster groups $[Nb_6I_8]$ in the compound Nb_6I_{11} are linked to one another by six intercluster bridging iodine atoms in three different directions; the $[Mo_6Cl_8]$ fragments in molybdenum dichloride are joined by four intercluster bridging chlorine atoms in two directions, so that layers of interlinked cluster groups with two terminal chlorine atoms are formed; finally, a structure with isolated molecular fragments, where, in contrast to the first two examples, all the ligands L are terminal, obtains in molybdenum dibromide dihydrate, so that there are no bridge bonds at all between the cluster groups $[Mo_6Br_8]$ in the $[Mo_6Br_8]Br_4.2H_2O$ crystal.

Instances of more complex bridges linking cluster groups are also encountered. Thus the $[W_6Br_8]Br_6$ cluster complexes in crystals of the tungsten bromide W_6Br_{16} are linked into chains by additional Br_2 bridging groups,[59] while in W_6Br_{18} such complexes are linked by Br_2 bridging groups in two directions, which leads to the formation of layers[60] (Fig.6).

Table 4. Coordination of the ligands L to the metal atoms of the $[M_6X_8]$ cluster group.[5]

Compound	$[M_4X_4]L_4$	Total number of ligands in molecules	Number of intercluster bridging μ_2-ligands
$Mo_6Br_{12}.2H_2O$	$[Mo_6Br_8]Br_4(H_2O)_2$	14	0
$Cs_2Mo_6Br_{14}$	$[Mo_6Br_8]Br_6$	14	0
$CsMo_6Br_{13}$	$[Mo_6Br_8]Br_4Br_{2/2}$	13	2
Mo_6Br_{12}	$[Mo_6Br_8]Br_2Br_{4/2}$	12	4
Nb_6I_{11}	$[Nb_6I_8]I_{6/2}$	11	6

Depending on the type of ligand, their number, charge, and the character of the bonding (terminal or bridging), the complexes $[M_6X_8]L_6$ can be either negatively charged species (behaving as anions in compounds of involved composition) or uncharged.

The change to structures with bridging ligands following a decrease in the number of ligands per M_6 cluster is illustrated in Table 4. The limiting composition of a cluster compound with six simple μ_2-bridging intercluster L ligands is described by the formula $[M_6X_8]L_{6/2}$. The lower niobium iodide Nb_6I_{11}, for example, has this composition.

(b) Octahedral Clusters in Chalcogenide Systems

Octahedral cluster groups are characteristic also of binary and ternary molybdenum chalcogenides.[61,62] For example, in the lower molybdenum selenide and telluride having the analytical formula Mo_3Y_4 the main structural fragment is the $[Mo_6Y_8]$ cluster group. In the Mo_3Se_4 structure the $[Mo_6Se_8]$ cluster fragments are arranged in such a way that the molybdenum atoms of one cluster group interact with the selenium atoms of the neighbouring groups (Fig.7*a*).[63] If this case is then treated in terms of the idea that complexes of the type $[M_6Y_8]L_6$ are formed, then the Mo_6Se_8 binary phase can be described by the crystal-chemical formula $[Mo_6Se_2Se_{6/2}]Se_{6/2}$, which implies that six Y ligands in the $[M_6Y_8]$ cluster fragments function at the same time as the ligands L for other neighbouring cluster groups, i.e. behave simultaneously as intercluster bridges. This example demonstrates significant differences between the hexanuclear halide and chalcogenide clusters.

In the crystals of compounds belonging to the Mo_6Se_8 structural type the interaction of the Mo_6 metallic clusters with one another via direct metal–metal bonds is also observed (Fig.6*a*). Such interaction leads to the metallic character of the conductivity of these compounds and even to superconducting properties (MO_6Se_8 is a superconductor with T_c = 6.25 K).[11]

Another important feature of the Mo_6Se_8 structure is the existence of free channels between the cluster groups. When these channels are filled by atoms of various metals, it is possible to obtain a whole series of ternary chalcogenides having the general formula $M_xMo_6Y_8$ (Y = S or Se).[61] Such ternary chalcogenides, which have extremely interesting superconducting properties, have come to be called the Chevrel phases after one of the first investigators of substances of this class who still continues to work vigorously in the field of the chemistry of cluster compounds.[62]

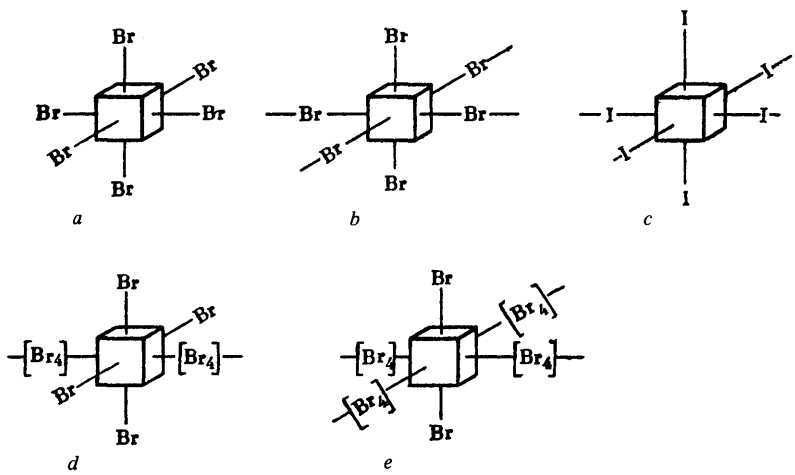


Figure 6. The intercluster bridging ligands in the octahedral transition metal halide complexes:[5] *a*) W_6Br_{14}; *b*) W_6Br_{12}; *c*) Nb_6I_{11}; *d*) W_6Br_{16}; *e*) W_6Br_{18}.

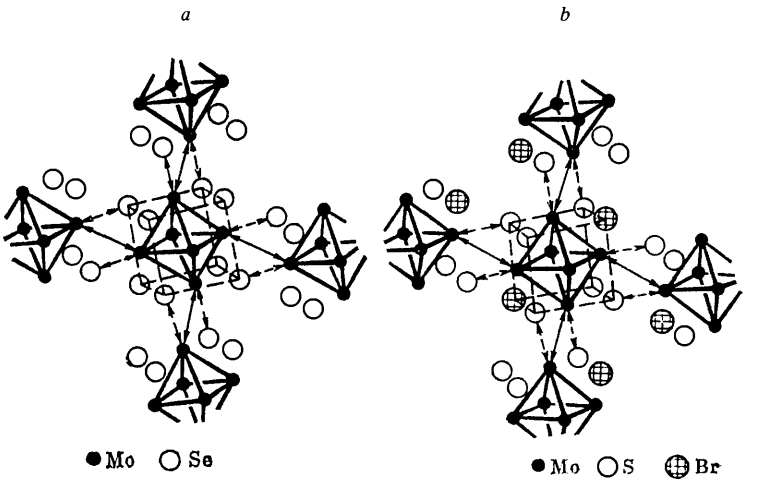


Figure 7. The structure of octahedral clusters: *a*) Mo_6Se_3;[63] *b*) $Mo_6S_6Br_2$.[78]

The chalcogenide cluster groups $[Mo_6Y_8]$, which are so characteristic of molybdenum compounds, have been unknown for other transition metals for a long time. Thus no mention whatever is made of octahedral clusters in a recently published review[64] devoted to the crystal chemistry of rhenium compounds with metal–metal bonds.

However, the most recent studies have shown that rhenium is also capable of forming octahedral cluster systems. Compounds having the composition $Mo_{6-x}Re_xY_8$ (Y = S or Se) and $Mo_4Re_2Te_8$, belonging to the Mo_6Se_8 structural type in which $Mo_{1.5}Re_{4.5}$ and Mo_4Re_2 heterometallic octahedral clusters are produced, were obtained in 1978.[65,66] Solid solutions having the composition $Mo_2Re_4S_{8-x}Se_x$ ($0 \leq x \leq 8$) and $Mo_2Re_4Se_{8-x}Te_x$ ($0 \leq x \leq 1.2$) have also been synthesised.[65]

On the other hand, octahedral rhenium clusters have been observed in the ternary sulphides $Cs_4Re_6S_{13}$,[67] $K_4Re_6S_{12}$, $Na_4Re_6S_{12}$,[68,69] $Li_4Re_6S_{11}$,[70] and finally $Sr_2Re_6S_{11}$ and $Ba_2Re_6S_{11}$.[71] The structure of ternary rhenium sulphides in which the $[Re_6S_8]$ cluster groups are linked to one another by μ_2-S and μ_2-S_2 bridging ligands (Figs.8*a* and 8*b*) are described by the following crystal-chemical formulae: $[Re_6S_8SS_{2/2}(S_2)_{3/2}]^{4-}$ (in $Cs_4Re_6S_{13}$), $[Re_6S_8S_{4/4}(S_2)_{2/2}]^{4-}$ (in $K_4Re_6S_{12}$ and $Na_4Re_6S_{12}$), and $[Re_6S_8S_{6/2}]^{4-}$ (in $Li_4Re_6S_{11}$).

The octahedral cluster is the principal structural fragment of the binary rhenium telluride which had been assumed to be a ditelluride for a long time. However, it has been shown convincingly[72] that the composition of this phase corresponds to the analytical formula Re_2Te_5. The crystal structure of rhenium telluride was determined by ourselves together with N.V.Podberezskaya and by Liu et al.;[73] the $[Re_6Te_8]Te_6$ cluster groups in the Re_2Te_5 structure are linked to one another by tellurium atoms (Fig.8*c*).

The first carbonyl compound containing an octahedral rhenium cluster with an incorporated carbon atom, i.e. $[Re_6(\mu_3\text{-}H)_2C(CO)_{18}]^{2-}$, has been obtained recently.[74]

Consequently the formation of hexanuclear cluster groups is characteristic of all the metals considered. However, niobium, tantalum, and tungsten compounds containing the $[M_6Y_8]$ (Y = S, Se, or Te) cluster groups are at present unknown; rhenium compounds where all the X atoms are halogens in the $[Re_6X_8]$ cluster groups have not been so far obtained either.

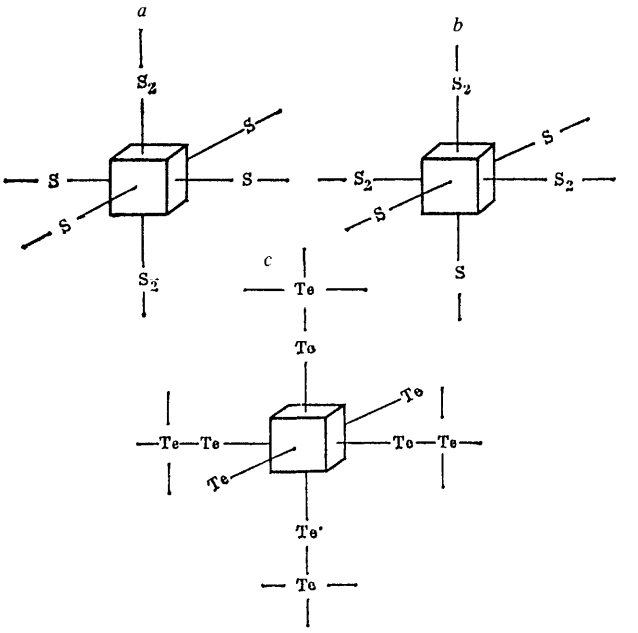


Figure 8. The intercluster bridging ligands in the octahedral rhenium chalcogenide clusters: *a*) $Na_4Re_6S_{12}$;[69] *b*) $Cs_4Re_6S_{13}$;[67] *c*) Re_6Te_{15}.[73]

Since the $[M_6X_8]$ and $[M_6Y_8]$ halide and chalcogenide cluster groups have virtually identical structures, the possibility of the formation of similar groups with mixed ligands, i.e. chalcogenide halides, is indicated; such groups in the cubane $X_{8-n}Y_n$ would contain halogen and chalcogen atoms simultaneously. The similarity of the crystal-chemical characteristics of the halogen and chalcogen atoms makes it possible to replace one ligand by another without a significant alteration in the structure of the cluster groups. Naturally, one must

bear in mind that the halogen and chalcogen atoms have different electron-accepting capacities; the electron density on the M_6 cluster therefore changes significantly following an alteration of the ligand environment of this kind, which should lead to a change of many properties of the compounds considered.

(c) Cluster Octahedral Molybdenum Chalcogenide Halides

The molybdenum chalcogenide halides Mo_6YX_{10} (Y = S, Se, or Te; X = Cl, Br, or I) belong to the Nb_6I_{11} structural type (space group P_{ccn}, orthorhombic system, $Z = 4$).[75,76] The unit cell parameters of these compounds are presented in Table 1.

The structure of the compounds has been established by the X-ray diffraction of Mo_6SeCl_{10} single crystals.[76] The crystal-chemical formula of the compounds Mo_6SeCl_{10} is $[Mo_6SeCl_7]Cl_{4/2}Cl_{2/2}$. The $[Mo_6SeCl_7]$ cluster groups are linked by four bridging chlorine atoms: two other bridging chlorine atoms link the layers to one another. The selenium atom enters into the composition of the $[Mo_6Y'_8]^+$ cluster fragment (Fig. 9*a*). The non-equivalence of the μ_3-ligands in $[Mo_6SeCl_7]$ results in the C_i symmetry of the Mo_6 cluster in Mo_6SeCl_{10}; this is the lowest symmetry among all the known octahedral clusters present in other phases with $[Mo_6Y_8]$ groups. The Mo–Mo distances in the Mo_6 cluster are in the range 2.598–2.626 Å.

As was to be expected, the Mo–Y′ distances (2.468–2.516 Å) in the $[Mo_6Y'_8]$ cluster group are somewhat greater than the average Mo–(μ_3-Cl) distance (amounting to approximately 2.46 Å) in the $[Mo_6Cl_8]$ cluster group of the corresponding chloride complexes[55] and are appreciably less than the Mo–(μ_3-Se) distances (2.52–2.58 Å) in Mo_6Se_8, which can be attributed to a different oxidation state of selenium in Mo_6SeCl_{10} than in Mo_6Se_8.

The distances between the molybdenum atoms and the six bridging chlorine atoms linking the $[Mo_6Y'_8]$ cluster groups with one another are in the range 2.494–2.534 Å, which is close to the analogous distance in molybdenum dichloride (2.49 Å).[57] Each molybdenum atom in the $[Mo_6Y'_8]$ group is at a distance of 0.09 Å from the corresponding face of the Y'_8 pseudocube (the plane passing through the four Y′ atoms); this results in the formation of a greatly flattened square pyramid.

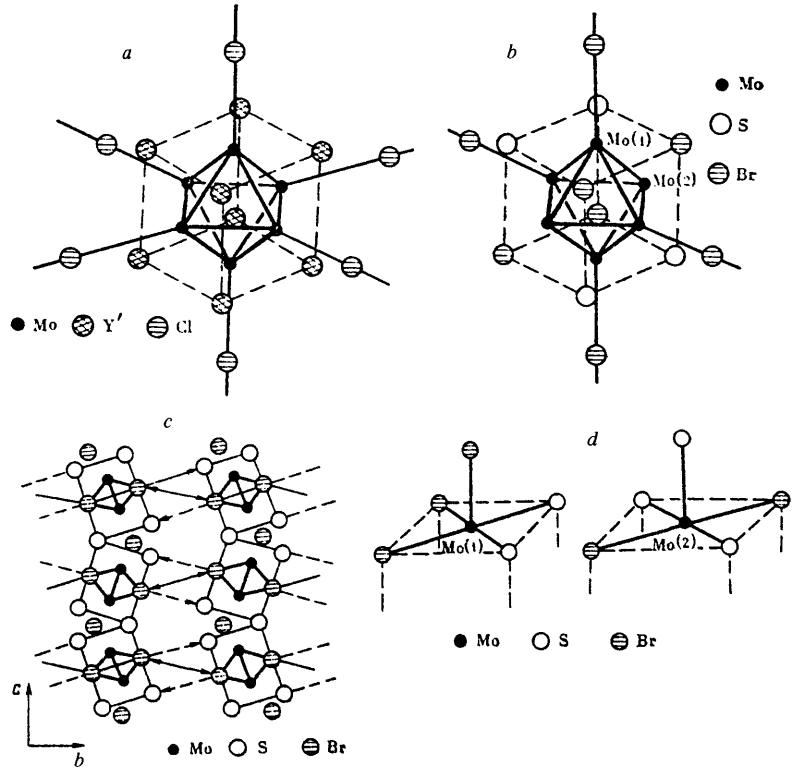


Figure 9. The structure of the hexanuclear molybdenum chalcogenide halides: *a*) a fragment of the Mo_6SeCl_{10} structure;[76] *b*) a fragment of the $Mo_6S_3Br_6$ structure;[77] *c*) three-dimensional packing of $Mo_6S_3Br_6$;[77] *d*) the difference between the coordinations of the molybdenum atoms in $Mo_6S_3Br_6$.[77]

†In this complex sevel Cl atoms and one Se atom are distributed statistically among the eight Y′ poistions of the Mo_6 coordination sphere.

The sulphide bromide $Mo_6S_3Br_6$ crystallises in the orthorhombic system (space group *Cmcm*, $Z = 4$; the unit cell parameters are presented in Table 1).[77] $Mo_6S_3Br_6$ has a layer structure, which represents a new structural type of cluster compounds containing the $[Mo_6Y'_8]$ group.

The principal structural motif of $Mo_6S_3Br_6$ is the $[Mo_6S_4Br_4]$ cluster group in which the sulphur and bromine atoms are ordered and are arranged in pairs along the diagonally opposite edges of the Y'_8 pseudocubane (Fig. 9*b*). All the bromine atoms in $[Mo_6S_4Br_4]$ belong to one cluster group and constitute μ_3-ligands usual for such structures. However, the sulphur atoms in $[Mo_6S_4Br_4]$ are non-equivalent. The two sulphur atoms located on one spatial diagonal are μ_4-ligands: they are linked to three molybdenum atoms in the given cluster group and in addition react with the molybdenum atom of the neighbouring cluster group in the direction of the *b* axis. The other two sulphur atoms are μ_6-ligands, linking two Mo_6 clusters of two neighbouring $[Mo_6S_4Br_4]$ cluster groups, which are thus linked to one another via a common sulphur atom. Consequently the principal structural motif of $Mo_6S_3Br_6$ can be described by the crystal-chemical formula $[Mo_6S_{2/2}S_{2/2}Br_4]$.

In each such group the four molybdenum atoms lying in one plane are coordinated to four bridging bromine atoms, which connect the $M_6Y'_8$] fragments in pairs. As a result, an infinite molecular chain of the $[M_6Y'_8]$ cluster groups joined by the common vertices of the pseudocubanes Y'_8 is formed in a direction parallel to the *c* axis. It can be described by the crystal-chemical formula $[Mo_6S_{2/2}S_{2/2}Br_4]Br_{4/2}S_{2/2}$.

The molecular chains extended along the *c* axis interact with one another in the direction of the *b* axis via the Mo–S bonds 2.503 Å long and Mo–Mo bonds 3.536 Å long. This results in the formation of layers parallel to the *bc* plane with a weak interaction also along the *a* axis. The Br...Br distances between the layers are in the range 3.634–3.742 Å and are close to the usual length of the van der Waals contacts between bromine atoms (Fig. 9*c*).[17]

The molybdenum atoms in $Mo_6S_3Br_6$ are crystal-chemically non-equivalent (Fig. 9*d*). The Mo(1) atoms are coordinated to three bromine atoms and two sulphur atoms via the vertices of a tetragonal pyramid, while the Mo(2) atoms are coordinated via two bromine atoms and three sulphur atoms, the sulphur atoms located at the vertex of the pyramid belonging to a neighbouring $[Mo_6S_4Br_4]$ fragment.

The Mo_6 cluster in $Mo_6S_3Br_6$ has the C_{2h} symmetry and the Mo–Mo distances are in the range 2.63–2.68 Å. These distances are intermediate between those observed in the Mo_6Se_8 and $Mo_6Br_{12}.2H_2O$ crystals.

Each molybdenum atom is located over the corresponding face of the S_4Br_4 pseudocubane, so that a flattened tetragonal pyramid with the molybdenum atom at the apex is formed. The Mo(1) atoms is at a distance of 0.10 Å from the S_2Br_2 plane, while the Mo(2) atom is virtually in the plane [the distance from the S_2Br_2 plane to Mo(2) is only 0.02 Å].

The molybdenum sulphide halides $Mo_6S_6Br_2$ and $Mo_6S_6I_2$ crystallise in the orthorhombic system (Mo_6Se_8 structural type; space group $\bar{R}3$, $Z = 1$; the unit cell parameters of these compounds are listed in Table 1).[78]

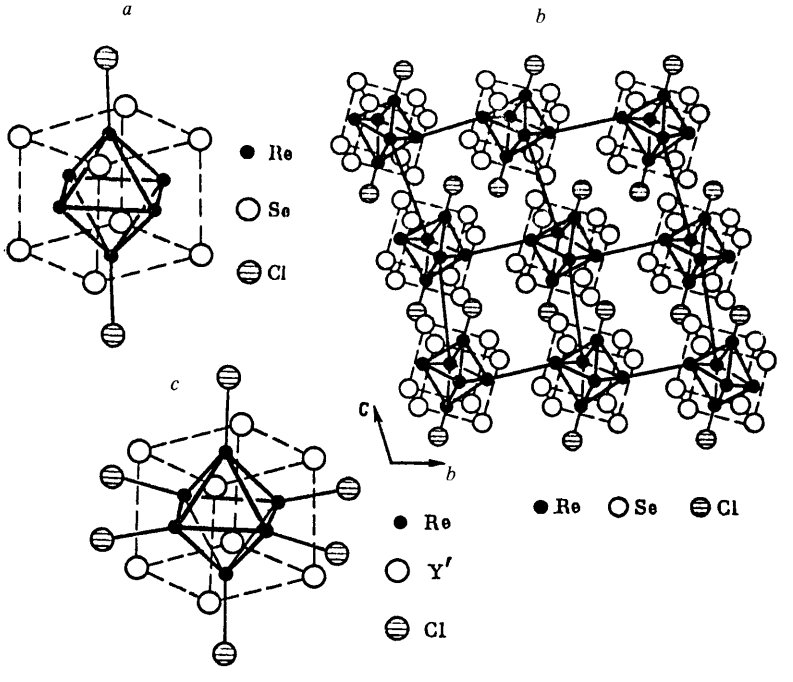


Figure 10. The structure of the hexanuclear rhenium chalcogenide halides: *a*) a fragment of the $Re_6Se_8Cl_2$ structure;[79] *b*) three-dimensional packing of $Re_6Se_8Cl_2$;[79] *c*) a fragment of the $Re_6Se_4Cl_{10}$ structure.[80]

The structure of the molybdenum sulphide bromide $Mo_6S_6Br_2$ resembles that of Mo_6Se_8.[78] An octahedron made up of molybdenum atoms is inscribed in the somewhat distorted pseudocubane S_6Br_2, the opposite two vertices of which are occupied by bromine atoms in such a way that each molybdenum atom is located above the centre of the face outside the cube at a distance of 0.18 Å. The Mo_6 octahedral cluster with D_{3h} symmetry is characterised by two independent Mo–Mo distances of 2.719 and 2.732 Å. While the Mo_6 octahedron in $Mo_6S_6Br_2$ is close to ideality, the S_6Br_2 pseudocubane in this structure is highly distorted (Fig. 7*b*).

The most important feature of the $Mo_6S_6Br_2$ structure is the fact that the halogen atoms in the cluster group are ordered and occupy two *c* positions in the direction of the threefold rhombohedral axis. This factor in fact leads to the formation of compounds with the given stoichiometry.

The interaction of the $[Mo_6Y_8]'$ motifs in the crystal takes place via the bonds between the molybdenum atoms and the sulphur atoms in other cluster groups; the length of such bonds is 2.485 Å (Fig. 7*b*). Thus the molybdenum sulphide bromide $Mo_6S_6Br_2$ has the crystal-chemical formula $[Mo_6S_{6/2}Br_2]S_{6/2}$.

Molybdenum sulphide halides have high temperatures corresponding to the transition to the superconducting state (T_c = 13.8 K for $Mo_6S_6Br_2$ and T_c = 14.0 K for $Mo_6S_6I_2$). It has been suggested that[61] the appearance of superconductivity is associated with the interaction of the molybdenum atoms belonging to neighbouring octahedral clusters and located at a distance of 3.225 Å from one another.

(d) Octahedral Cluster Rhenium Chalcogenide Halides

The rhenium selendie chloride $Re_6Se_8Cl_2$ crystallises in the triclinic system (space group $P\bar{1}$, $Z = \bar{1}$; the unit cell parameters are listed in Table 1).[79] The crystal structure of $Re_6Se_8Cl_2$ (Fig. 10) can be described as one made up of $[Re_6Se_8]Cl_2$ motifs.[79] These motifs consist of Re_6Se_8 cluster groups, which are coordinated above and below to two terminal chlorine atoms via bonds with two rehnium atoms located on the opposite faces of the Se_8 cube (the Re–Cl distance is 2.37 Å).

The $[Re_6Se_8]Cl_2$ fragments in the crystal are arranged in layers parallel to the *ab* plane. The interaction of the cluster groups in such layers takes place via the Re–Se bonds. Four rhenium atoms in each $[Re_6Se_8]$ cluster group are linked to the selenium atoms belonging to four neighbouring $[Re_6Se_8]$ fragments. The lengths of these Re–Se bonds is 2.65 Å, which differs little from that observed in $[Re_6Se_8]$, which is 2.5–2.6 Å. This arrangement is described by the crystal-chemical formula $[Re_6Se_{4}Se_{4/2}]Cl_2Se_{4/2}$. The Re...Re distances between neighbouring clusters within the layer are 3.41 and 3.44 Å (the Re–Re distances in the Re_6 cluster are in the range 2.62–2.66 Å).

The interaction of the $Re_6Se_8Cl_2$ molecular layers in the direction of the *c* axis is insignificant and takes place via the Se...Cl bonds over distances of 3.17 and 3.45 Å. This character of the interaction of the layers determines the quasi-two-dimensional properties of the crystal structure $Re_6Se_8Cl_2$.

The rhenium chalcogenide halides $Re_6Y_4X_{10}$ (Y = Se or Te; X = Cl or Br) crystallise in the triclinic system (space group $P\bar{1}$, Z = 2). The crystal structure has been determined for $Re_6Se_4Cl_{10}$ single crystals[80] (Fig. 10*c*). The rhenium selenide chloride consists of molecular crystals and the Re_6 octahedral clusters in the structure are not linked by intercluster bridging ligands, so that the crystal-chemical formula is $[Re_6Se_4Cl_4]Cl_6$. Two independent cluster fragments are located at the centres of inversion. The Re–Re distances in the octahedral Re_6 cluster are 2.601–2.618 Å. An interesting feature of this structure is the fact that the Se and Cl atoms behave as μ_3-ligands in the $[Re_6Se_4Cl_4]$ cluster group. Although an unambiguous determination of their positions is difficult, the variant where the Se_4Cl_4 pseudocubane is made up of two interpenetrating Se_4 and Cl_4 tetrahedra is the most likely. The model with the X and Y atoms at the opposite vertices of the cubane is well correlated with the spectroscopic properties of the compounds.[80]

(e) The Crystal-chemical Features of the Octahedral Cluster Molybdenum and Rhenium Chalcogenide Halides

In discussing the crystal-chemical features of the structures of the octahedral cluster chalcogenide halides, it is essential in the first place to note, as a general feature, the tendency of the $[M_6Y_8']$ cluster groups to form complexes of the type $[M_6Y_8']L_6$. If the total number of ligands (Y' + L) is 14 per M_6 cluster, then structures with isolated $[M_6Y_8']L_6$ complexes are formed as in the halide systems. This is clearly seen in relation to the rhenium chalcogenides $[Re_6Y_4X_4].X_6$ as an example, which are characterised by a molecular type of structure. With decrease of the number of ligands, the complexes $[M_6Y_8']L_6$ are formed as a result of the coordination at the L site of atoms belonging to other cluster groups. However, in contrast to the halide system discussed above, where ligands of type L constitute common intercluster bridges, in the chalcogenide halides this function is fulfilled by the Y' atoms, i.e. the atoms which form part of the $[M_6Y_8']$ cluster group. The same simple behaviour is observed in this instance too: with decrease of the number of ligands per M_6 cluster, the number of atoms common to two neighbouring cluster groups increases and the Y' begin to assume the function of intercluster bridges. This rule is well illustrated by the data in Table 5: a steady variation of the character of the coordination is seen on passing from isolated molecular chalcogenide halides of the type $[Re_6Y_4X_4]X_6$ (14 ligands per cluster) to the $[Me_6S_{6/2}Br_2]S_{6/2}$ structure (eight ligands per cluster). Depending on the atoms in the Y_8' cubane through which the cluster groups are linked to one another, structures of different size can be produced.

Table 5. Variation of the intercluster metal–metal distances as a function of the type of bridging ligands.

Compound	$[M_4Y_8']L_6$	N_L^*	$\frac{R}{(M...M)}$, Å	Character of structure	Refs.
$Re_6Se_4Cl_{10}$	$[Re_6Se_4Cl_4]Cl_6$	14	3.69	molecular	[80]
Mo_6SeCl_{10}	$[Mo_6SeCl_7]Cl_{6/2}$	11	3.687	polymeric (three-dimensional)	[76]
$Re_6Se_6Cl_2$	$[Re_6Se_4Se_{4/2}]Cl_2Se_{4/2}$	10	3.42	polymeric (layer)	[79]
$Mo_6S_3Br_6$	$[Mo_6S_{2/2}S_{2/2}Br_4]Br_{4/2}S_{2/2}$	9	3.536	polymeric (layer)	[77]
$Mo_6S_6Br_2$	$[Mo_6S_{6/2}Br_2]S_{6/2}$	8	3.225	polymeric (three-dimensional)	[78]
Mo_6S_8	$[Mo_6S_{6/2}S_2]S_{6/2}$	8	3.086	polymeric (three-dimensional)	[61]

*The number of ligands per cluster in the molecule.

It is also of interest ot note that the coordination of the ligands Y_8' changes on formation of such intercluster bridges: on formation of additional bonds, the μ_3-ligands beome μ_4-ligands and even μ_6-ligands (as has been observed in $Mo_6S_3Br_6$).

The character of the chemical bonds in octahedral cluster chalcogenide halides can apparently be described within the framework of the ionic-covalent model, where it is assumed that there is a covalent interaction between the metal atoms in the M_6 octahedron, while the bonds between the metal and the ligands are ionic. Calculations of the electronic structure of the hexanuclear metal halides and chalcogenides have convincingly confirmed the validity of this treatment.[22,61] An important feature of these systems consists in the fact that two groups of molecular orbitals are formed by the atomic *d* orbitals of the metal; 12 bonding MO (which describe 12 two-centre M–M bonds oriented along the edges of the octahedral M_6 cluster) are separated from the higher antibonding unoccupied MO.[81,82]

Consequently the formation of 12 simple two-electron M–M bonds in the M_6 cluster requires 24 valence electrons. This situation obtains in halide systems with the $[Mo_6X_8]^{4+}$ cluster group and also in the chalcogenide halides Mo_6YX_{10} and $Mo_6S_3Br_6$ (Table 6). However, in the $Mo_6S_6Y_2$ and also Mo_6S_8 chalcogenide halides the Mo_6 cluster is electron-deficient, which implies that the bonding MO, characterising the M–M interaction in the octahedral cluster, are only partly occupied. Consequently the Mo–Mo bond order should decrease in the series of compounds $Mo_6S_3Br_6 \rightarrow Mo_6S_6Br_2 \rightarrow Mo_6S_8$. A decrease of the number of valence electrons in the Mo_6 cluster entails an increase of the Mo–Mo distances (Table 6). Indeed the molybdenum sulphide Mo_6S_8, which has only 20 electrons per cluster, is thermodynamically unstable and cannot be obtained by direct synthesis from the elements. The addition of electrons to the electron-deficient cluster system stabilises the phases, which is clearly demonstrated by chalcogenide halides of the type of $Mo_6S_6Br_2$ and $Mo_6S_6I_2$ (22 electrons per cluster), and also by the $M_xMo_6S_8$ Chevrel phases, which can contain 21–24 electrons per cluster depending on the nature of the metal M. It has been shown convincingly for a large number of Chevrel phases that the interatomic Mo–Mo distances in the Mo_6 cluster depend on the number of valence electrons localised on the cluster.[61]

Table 6. Dependence of the Mo–Mo interatomic distances in the Mo_6 cluster on the number of valence electrons localised on the cluster.

Compound	R (Mo–Mo), Å	N_e^*	Refs.
$[Mo_6Cl_8]Cl_2Cl_{4/2}$	2.61	24	[59]
$Cs_2[Mo_6Cl_8]Br_6$	2.61	24	[76]
$Hg[Mo_6Cl_8]Cl_6$	2.62	24	[76]
$[Mo_6SeCl_7]Cl_{6/3}$	2.62	24	[76]
$[Mo_6Br_6]Br_4 \cdot 2H_2O$	2.64	24	[60]
$Mo_6S_3Br_6$	2.66	24	[77]
$Mo_6S_6Br_2$	2.73	22	[78]
Mo_6S_8	2.78	20	[61]

*The number of electrons per Mo_6 cluster.

Thus shorter distances between the molybdenum atoms in the Mo_6 cluster are observed in those compounds where the number of electrons per cluster approaches 24. The size of the Mo_6 octahedron can serve as a measure of the degree of occupation of the conductivity band. In the most highly contracted octahedron all the bonding states are occupied and the number of electrons per cluster is 24.

An interesting aspect of the crystal chemistry of the octahedral cluster chalcogenide halides is the variation of the shortest metal–metal distances between the clusters (Table 5). With increase of the number of bridging cross-links between the cluster groups, conditions arise for closer direct contacts between the metal atoms of neighbouring clusters. Thus the Mo–Mo distances between neighbouring clusters decrease steadily in the series of molybdenum chalcogenide halides Mo_6SeCl_{10}, $Mo_6S_3Br_6$, and $Mo_6S_6Br_2$: 3.687, 3.536, and 3.225 Å respectively.

The conducting properties of the binary and ternary chalcogenide containing the $[M_6Y_8]$ cluster groups are extemely interesting. The unique superconducting properties of the Chevrel phases are widely known.[11,62] They are determined mainly by the 4*d* electrons of molybdenum occupying the conductivity band. If the conductivity band is incompletely filled, favourable conditions arise for the appearance of superconductivity in such phases. The Mo–Mo distances between neighbouring clusters are then also significant.[61]

From this point of view, among the chalcogenide halides considered here the $Mo_6S_6Br_2$ and $Mo_6S_6I_2$ phases are of the greatest interest (22 electrons) per cluster. They are conductors and undergo a transition to the superconducting state at 13.8 and 14.0 K respectively.[78]

If the conductivity band is fully occupied, the compounds exhibit semiconducting or dielectric properties. For example, $Mo_6S_3Br_6$ and $Re_6Se_4Cl_{10}$, in which there are 24 valence electrons per cluster, can be included among such phases.

III. METHODS OF SYNTHESIS

The cluster niobium, molybdenum, and rhenium chalcogenide halides are usually obtained by the high-temperature synthesis involving prolonged heating of mixtures of different composition in evacuated sealed tubes: (a) metal + halogen + chalcogen; (b) metal chalcogenide + halogen; (c) metal halide + chalcogen; (d) metal halide + metal + chalcogen; (e) metal chalcogenide + metal halide; (f) metal + chalcogen halide. The initial substances are usually taken in proportions corresponding to the stoichiometry of the substance to be synthesised.

A general preparative method of synthesis of transition metal chalcogenide halides at high temperatures is that of gas-transport chemical reactions. A characteristic feature of these reactions, whereby it is possible to obtain high quality crystals, is mass transfer under the conditions of a temperature gradient with segregation of the solid phase in the cold zone; phases separated in space from the initial reaction mixture are then produced.[84]

(a) The Synthesis and Properties of Dinuclear Chalcogenide Halides

All the compounds having the composition $NbYX_3$ (Y = Se or Te; X = Cl, Br, or I) have been obtained by the high-temperature sealed tube synthesis from the elements. A stepwise increase of temperature with a final treatment at 800 °C for 3–4 days has been used. When a temperature difference is created at the ends of the sealed tube, mass transport and growth of acicular single crystals are observed.[16]

The chalcogenide halides $NbYX_3$ are stable in air; they form grey single crystals with metallic lustre. The thermal properties of these substances have been investigated.[16] The final product of the thermal decomposition of $NbTeI_3$ *in vacuo* is Nb_3Te_4.

Compounds having the analytical formula MYX_3 have been obtained also for other metals (M = Ta, Mo, or Re) by the interaction of the corresponding metal pentahalides with Sb_2Y_3 (Y = S or Se) in solution in CS_2.[85] However, the structure of these phases is unknown and at the present time

there are no grounds for assigning them to dinuclear compounds.

Compounds having the composition NbY_2X_2 (Y = S or Se; X = Cl, Br, or I) have been obtained by the sealed tube method in the 480–530 °C temperature gradient. The starting materials were metallic niobium, the elemental chalcogen, and niobium tetrahalides. The single crystals of niobium chalcogenide halides were grown in the cold zone of the sealed tube in the form of plates. The transport time was 3–4 weeks.[18] The compounds NbS_2Cl_2 and NbS_2Br_2 can be obtained on heating the metal in S_2Cl_2 and S_2Br_2 vapours.[86]

The compounds NbY_2X_2 are stable in air and are insoluble in the majority of solvents. On heating, they undergo polymorphic transformations (Table 1). The thermal decomposition of the compounds proceeds in different ways depending on the composition. For example, the compounds NbY_2X_2 (X = Cl or Br) decompose in accordance with the scheme

$$3NbY_2X_2\,(\text{solid}) \rightarrow NbY_2\,(\text{solid}) + X_2\,(\text{gas}) + 2NbYX_3\,(\text{gas}).$$

The chalcogenide iodides NbY_2I_2 dissociate via the reaction

$$NbY_2I_2 \rightarrow NbY_2\,(\text{solid}) + I_2\,(\text{gas}).$$

The compounds are diamagnetic and are semiconductors.[86]

Single crystals of the black sulphide chloride MoS_2Cl_3 have been obtained on heating to 450 °C a 1 : 10 mixture of $MoCl_3$ and S in S_2Cl_2.[19] A yellow-brown sulphide chloride of the same composition has been obtained on heating molybdenum pentachloride in S_2Cl_2 at 250 °C.[87] The structure of the black MoS_2Cl_3 has been established by X-ray diffraction[19] and the yellow-brown molybdenum sulphide chloride has been characterised only by infrared and Raman spectra.

Single crystals of the brown selenide chloride $Nb_3Se_5Cl_7$ have been obtained accidentally in a study of the transport of $NbSe_2Cl_2$ in the presence of $NbCl_4$ in a temperature gradient (at 535–525 °C). The transport time was 2–3 weeks.[20] The dark-blue bromide analogue $Nb_3Se_5Br_7$ has been obtained in the form of single crystals on heating a reaction mixture comprising $NbSe_2Br_2$ and $NbSeBr_3$. The authors noted a poor reproducibility of this syntheses.[20]

(b) The Synthesis and Properties of Trinuclear Chalcogenide Halides

The trinuclear chalcogenide halides $Mo_3Y_7X_4$ have been obtained in quantitative yields on heating the lower molybdenum halides MoX_2 and MoX_3 (X = Cl, Br, or I) in a sulphur or selenium melt at temperatures in the range 350–450 °C:[89–92]

$$6MoCl_3 + 24S \rightarrow 2Mo_3S_7Cl_4 + 5S_2Cl_2\ .$$

The excess chalcogen and the Y_2X_2 formed as a result of the reaction are removed by heating *in vacuo* or are washed out with CS_2.[89] Another convenient method of synthesis of the trinuclear molybdenum chalcogenide halides involves the conversion of the chalcogenide halide MoY_4X_2 (Y = S or Se; X = Br or I) on heating in sealed tubes:[93]

$$3MoS_4I_2 \rightarrow Mo_3S_7I_4 + 5S + I_2\ .$$

The cluster compounds $Mo_3Y_7X_4$ are insoluble in organic solvents and do not sublime *in vacuo*, which hinders their further purification.

$Mo_3S_4Cl_4$ single crystals have been obtained on heating molybdenum trichloride and sulphur at 450 °C in a sealed tube in the presence of S_2Cl_2.[19]

The thermal properties of the trinuclear molybdenum chalcogenide halides have been investigated. Heating of $Mo_3Y_7X_4$ *in vacuo* or in an inert atmosphere results in the formation of their corresponding dichalcogenides.[89–92]

The process has a stepwise character in an atmosphere of hydrogen; the final reduction products at model temperatures are also dichalcogenides.[89–92]

(c) The Synthesis and Properties of Tetranuclear Chalcogenide Halides

The tetranuclear chalcogenide halides $M_4Y_4X_4$ (M = Nb or Mo; Y = S or Se; X = Cl, Br, or I) have been obtained by high-temperature annealing in evacuated quartz tubes, the reaction mixture consisting of the metal, the chalcogen, and a lower metal halide.

The niobium chalcogenide halides $Nb_4Y_4X_4$ have been obtained from Nb_3X_8, metallic niobium, and the chalcogen in a two-zone furnace with a temperature gradient of 700–800 °C.[45] The molybdenum sulphide halides $Mo_4S_4X_4$ have been synthesised at 1100 °C and the reaction mixture consisted of the corresponding dihalide, molybdenum, and sulphur.[46,47]

The tetranuclear niobium and molybdenum chalcogenide halides are stable in air and are insoluble in the usual organic solvents.

(d) The Synthesis and Properties of Hexanuclear Chalcogenide Halides

Practically all chalcogenide halides of this type are obtained via solid-phase synthesis reactions using high temperatures. The only exception is $Re_6Te_4Br_{10}$, which can be obtained by the reaction of rhenium telluride with bromine even at room temperature. The reason why the reaction proceeds under such mild conditions is apparently that the initial rhenium telluride Re_6Te_{15} already contains the octahedral Re_6 cluster in its structure. The lower halides, the chalcogen, and the metal in stoichiometric amounts are used as the starting reactants for the synthesis of compounds with a high metal content.

The compounds Mo_6YX_{10} (Y = S, Se, or Te; X = Cl or Br) have been obtained by the sealed tube method, the stoichiometric amounts of $MoX_2(MoX_3)$, Mo, and Y being sintered at temperatures in the range 1000–1150 °C for 24 h with subsequent reannealing under the same conditions.[76] Single crystals suitable for X-ray diffraction studies grow during the synthesis. The colour of the single crystals of the chalcogenide halides Mo_6YX_{10} varies from red to dark-brown depending on the composition. The compounds are stable in air, are diamagnetic, and are dielectrics.

The molybdenum sulphide bromide $Mo_6S_3Br_6$ has been obtained by the sealed tube synthesis, in which stoichiometric amounts of the $3MoBr_2$ + 3Mo + 3S powders, pressed into discs, are heated at 1200 °C for 24 h. The preparation of single-phase specimens requires reannealing under the same conditions after mixing the reaction products. $Mo_6S_3Br_6$ single crystals in the form of black lustrous plates grew at 1250 °C.[77]

The chalcogenide halides $Mo_6S_6Br_2$ and $Mo_6S_6I_2$ have been obtained by the sealed tube method. Stoichiometric amounts of powdered MoX_2, molybdenum, and sulphur were pressed into discs and the reaction was carried out at 1050 °C for 24 h. After mixing the reaction products, the latter were reannelaed under the same conditions.[78] The possible admixtures in this method of synthesis of the sulphide halides $Mo_6S_6X_2$ can be the Mo_2S_3 and $Mo_4Y_4X_4$ phases. In the synthesis of $Mo_6S_6I_2$ one can also begin with a mixture of stoichiometric amounts of the elements.[94] The attempts to obtain molybdenum sulphide chlorides having the same composition were unsuccessful.

The compounds are weakly paramagnetic and exhibit metallic conductivity. On decrease of temperature, they pass to the superconducting state, the width of the transitional region amounting to 1–2 K. The critical temperatures are 13.8 K for $Mo_6S_6Br_2$ and 14.0 K for $Mo_6S_6I_2$.[78]

The interaction of $Mo_6S_6I_2$ with copper has been investigated.[94] It has been established that single-phase products having the composition $Cu_xMo_6S_6I_2$, where $0 < x < 1.2$, which are isostructural with $Mo_6S_6I_2$, can be obtained at 470 °C. With increase of the amount of copper in the $Cu_xMo_6S_6I_2$ phases, the size of the unit cell increases somewhat but the temperature of the transition to the superconducting state decreases.

The rhenium selenide chloride $Re_6Se_8Cl_2$ has been obtained by the sealed tube method at 1000 °C from a mixture of $ReCl_5$, Re, and Se.[79] The compounds $Re_6Se_4Cl_{10}$ and $Re_6Se_4Br_{10}$ are obtained by the sealed tube method in which the $ReSe_2$ + $2ReX_5$ (X = Cl or Br) reaction mixture is heated at 700–750 °C for 10–15 h (the rhenium trihalide is taken in a slight excess). The reaction products are separated by vacuum-thermal distillation.[95] The rhenium selenide bromide $Re_6Se_4Br_{10}$ is also obtained by brominating $ReSe_2$ at 650–700 °C.[96]

The compound $Re_6Te_4Br_{10}$ is obtained by brominating the rhenium telluride Re_6Te_{15} with liquid bromine. The reaction proceeds even at room temperature, but the temperature is raised to 50–60 °C to achieve a more rapid completion of the process.[96]

IV. CHEMICAL PROPERTIES

As shown in the previous sections of the review, molecular structures with a metal–metal bond are not characteristic of the chalcogenide halides—the M_n cluster nuclei are linked into infinite chains, layers, or give rise to three-dimensional structures. Such polymeric structure of the cluster chalcogenide halides is manifested in their properties: their volatility is low and they are insoluble in organic solvents, which greatly hinders the study of their chemical properties. These compounds are as a rule stable in air and their reactivity is low.

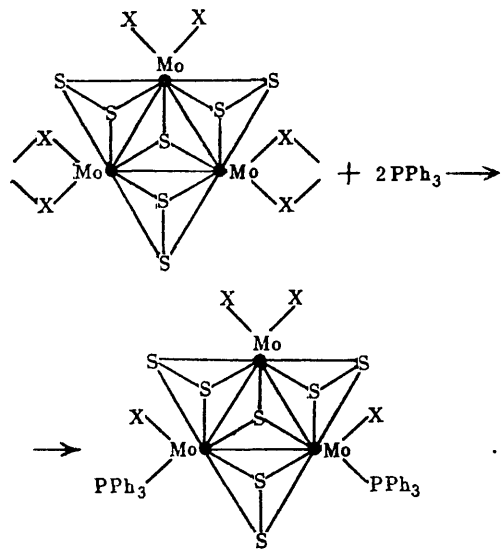
Related structural motifs arise in the cluster transition metal halides, chalcogenides, and chalcogenide halides. The chalcogenide halides occupy an intermediate position between the metal halides and chalcogenides. The cluster metal chalcogenides are frequently soluble in organic solvents, undergo complex formation reactions, and, as shown recently in relation to rhenium trihalides,[97] they enter into organometallic synthesis reactions. The cluster chalcogenides are chemically inert and decompose on treatment with strong oxidants or reductants under severe conditions.

We shall consider what synthetic approaches are possible in the study of the chemical properties of cluster chalcogenide halides. In our view, it is initially necessary to find ways of dissolving the cluster chalcogenide halides. The synthetic methods of the chemistry of complex and organometallic compounds are applicable to clusters soluble in organic solvents. In order to achieve the dissolution of the compounds, it is necessary to find reagents in the presence of which one-, two-, or three-dimensional structures are disrupted, but the main cluster fragments should persist. Monomeric structures in the cluster chalcogenide halides are usually formed with the aid of bridging halogen and chalcogen atoms or via the metal–metal intercluster interaction. The ways used to disrupt such different structures should apparently also be different.

We shall now turn to analogies from the chemistry of cluster metal halides. The reactions of hexanuclear cluster niobium, tantalum, molybdenum, and tungsten halides as well as the trinuclear rhenium halides with oxygen, sulphur-, nitrogen-, and phosphorus-containing ligands are well known. As a result of such reactions, the polymeric structures are broken up and molecular cluster complexes of metal halides with various ligands are formed, for example:[5,98]

$$Mo_6Cl_{12} + 2Et_3N \rightarrow Mo_6Cl_{12} \cdot 2Et_3N \ ;$$
$$Re_3Cl_9 + 3PPhEt_2 \rightarrow Re_3Cl_9 \cdot 3PPhEt_2 \ .$$

It has been shown recently[99] that the polymeric cluster sulphide halides $Mo_3S_7Cl_4$ and $Mo_3S_7Br_4$ interact with triphenylphosphine on heating in acetonitrile or benzonitrile, giving rise to molecular trinuclear complexes soluble in organic solvents:



The reaction of molybdenum sulphide chloride with PPh_3 in proportions of 1 : 5 produces a molecular complex having a different composition:

$$Mo_3S_7Cl_4 + 5PPh_3 \rightarrow 3S{=}PPh_3 + Mo_3S_4Cl_4 \cdot 2PPh_3 \ .$$

The formation of the triphenylphosphine sulphide can be accounted for by the elimination of sulphur atoms from the disulphide group. Reactions leading to the elimination of a chalcogen atom from the dichalcogenide group on treatment with various nucleophiles are convenient models for the understanding of many biochemical processes.[100]

Reactions involving the nucleophilic substitution of halogen atoms are of independent interest. Such reactions have been known for a long time for the cluster transition metal halides. For example, it has been shown for rhenium trihalides that the intercluster halogen atoms are the first to be involved in the substitution reaction with nucleophiles.[101] The first instance of the nucleophilic substitution of the halogen has been found for the cluster chalcogenide halides. The sulphide chloride $Mo_3S_7Cl_4$ interacts with sodium polysulphide with retention of the trinuclear cluster framework:[102]

$$Mo_3S(S_2)_3Cl_4 \xrightarrow[S_2^{2-}]{} [Mo_3S(S_2)_6]^{2-} \ .$$

Thus the first examples of the conversion of polymeric molybdenum chalcogenide halides into molecular clusters soluble in organic solvents have been found, which leads to wide possibilities for the investigation of the properties of compounds of this class.

In conclusion we may note that the study of the chemical properties of cluster transition metal chalcogenide halides may promote the solution of one of the most interesting problems in modern chemistry: Cotton has pointed out[4] the necessity for

the mutual approach of two fields of the chemistry of cluster compounds which have been largely developing independently, namely those concerned with the study of high valence clusters (the clusters with acido-ligands) and low-valence clusters (organometallic clusters). It may be that the cluster transition metal chalcogenide halides discussed in this review will prove important starting compounds for organometallic synthesis reactions, including reactions involving reactive cyclopentadienyl compounds of metals.

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Tetrafluoroammonium Salts

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The methods of synthesis, structure, thermal and chemical properties, and possible applications of tetrafluoroammonium salts have been reviewed.
The bibliography contains 76 references.

CONTENTS

I. Introduction 426
II. Synthesis of tetrafluoroammonium salts 426
III. Properties of tetrafluoroammonium salts 431

I. INTRODUCTION

Until the early nineteen-sixties, apparently, there were no theoretical or experimental indications of the possible existence of the NF_4^+ cation in the gas phase or in salt crystal lattices. The formula NF_4^+ appeared for the first time in Ref.1, where the dissociation energies and ionisation potentials of various fluorides were estimated, and it was concluded that salts of the NF_4^+ cation could not be obtained. Three years later, Wilson[2] devoted a special paper to the estimation of the stability of the NF_4^+ cation and its salts. He used the method of analogies, isoelectronic series, and the bond energy and ionisation potential values then available to estimate the crystal lattice energies of tetrafluoroammonium fluoride, perchlorate, sulphate, and tetrafluoroborate. The calculations showed that the first three salts should be extremely unstable relative to their possible decomposition products ($NF_3 + F_2$, $NF_3 + FClO_4$, $2NF_3 + F_2O + SO_3$ respectively) and cannot exist, and that the tetrafluoroborate may be stable at temperatures below 120 K. The possible stabilisation of the NF_4^+ cation in compounds with other polyatomic fluoro-anions was not examined,[2] although it was assumed that tetrafluoroammonium fluoroantimonate or fluoroarsenate might be more stable.[3]

Nitrogen trifluoride is extremely inert towards Lewis acids. An infrared spectroscopic study[4] of the reaction of nitrogen fluorides with Lewis acids established only weak association in the systems $NF_3 + BF_3$ (at temperatures below 148 K) and $NF_3 + BCl_3$ (below 173 K) and no association or reaction in the $NF_3 + PF_5$ system (as far as 145 K). The possible reaction $NF_3 + F_2 \rightleftharpoons NF_4^+ + F^-$ between NF_3 and fluorine in anhydrous hydrogen fluoride was noted in Ref.5. The authors of Ref.6, who studied the action of the bremsstrahlung of electrons on a number of compounds of fluorine, nitrogen, and oxygen, including a mixture of NF_3 and BF_3, were apparently close to the synthesis of NF_4^+.

In 1966, two groups of American authors[7,8] simultaneously reported the synthesis of two tetrafluoroammonium salts, the fluoroarsenate and the fluoroantimonate. In 1970, a method for preparing tetrafluoroammonium tetrafluoroborate was patented[9] in the USSR, and a paper[10] published in the same year described the properties of this compound, whose thermal stability was found to be much higher than that predicted in Ref.2. New methods for synthesising NF_4BF_4, NF_4AsF_6, and NF_4SbF_6 have since been found, and methods have been developed for preparing other tetrafluoroammonium salts. The synthesis of NF_4ClO_4 was reported[11] in 1980. The existence of this salt contradicts the predictions of Ref.2; it decomposes slowly only at 273 K.

The names "perfluoroammonium", "tetrafluoroammonium", "tetrafluoronitrogen", and "tetrafluoronitronium" have been proposed for the NF_4^+ cation. None of them can be regarded as satisfactory, but most authors prefer to call this ion the tetrafluoroammonium ion. This name will be used in the present work, but it must be borne in mind that the NF_4^+ ion cannot be obtained by replacing the hydrogen atoms in the ammonium ion, and that the formal oxidation state of nitrogen in NF_4^+ is +5, whereas that in NH_4^+ is -3. In the text, the name of the NF_4^+ ion will be abbreviated to TFA. The synthesis and properties of TFA salts were examined briefly in Refs.12 and 13.

II. SYNTHESIS OF TETRAFLUOROAMMONIUM SALTS

As shown below, the synthesis of TFA salts involves considerable experimental difficulties, and a special method of synthesis has to be developed for almost every new compound. This probably explains why TFA salts have as yet been prepared in only a few laboratories. In the present work, the experimental conditions for the synthesis of TFA salts will be examined in more detail than is usual in review papers; the "key" compounds, that is the hexafluoroarsenate, hexafluoroantimonate, and tetrafluoroborate, will be considered first, followed by the others in order of increasing atomic number of the central atom of the anion. The "key" TFA salts were synthesised first, and subsequently used to obtain various other TFA salts. The total number of TFA salts synthesised by mid-1983 was greater than 30.

$NF_4^+AsF_6^-$. This salt was first obtained[8,14] by the action of an electrical glow discharge on a mixture with the molar ratio $NF_3:AsF_5:F_2 = 1:1:2$. The method of synthesis is described in more detail in Ref.15. A mixture of NF_3, AsF_5, and F_2 was passed into a glass electrical-discharge reaction vessel, supplied from a transformer and fitted with a circulating pump, to an initial pressure of not more than 80 mmHg, after which the discharge was switched on and the reaction carried out under circulation conditions at a temperature of the walls of the reaction vessel of 195 K. The apparatus used had a low efficiency, and the synthesis of 1 g of salt took ~40 h. The same paper[15] described an unsuccessful attempt to obtain NF_4AsF_6 from NF_3, AsF_5, and an excess of F_2 by heating the reagents to 758 K at a pressure of ~168 atm in a Monel metal vessel for 12 h. Instead of the expected product, this gave $Ni(AsF_6)_2$, formed by corrosion of the walls of the autoclave.

According to Ref.3, however, when a mixture of NF_3, F_2, and AsF_5 was heated for a longer time (260 h) at 398 K, 95% pure NF_4AsF_6 was obtained. It was later established[16] that the NF_4AsF_6 specimens obtained by the high-temperature method do not have a uniform composition and contain appreciable quantities of nickel and copper salts, formed by corrosion of the walls of the Monel metal reaction vessel; salts of the $As_2F_{11}^-$ anion are not formed under these conditions.

TFA hexafluoroarsenate can be obtained photochemically.[17] Irradiation of an equimolar mixture of NF_3, F_2, and AsF_5, placed in a sapphire reaction vessel at room temperature, with a high-pressure mercury lamp (without a filter) gives NF_4AsF_6 in less than 1% yield. This low yield can be attributed to the deposition of a layer of product on the walls of the reaction vessel, leading to the absorption of ultraviolet radiation, and the low thermal stability of possible intermediate products of the photosynthesis. In an improved procedure,[18] NF_4AsF_6 was obtained by the ultraviolet irradiation of NF_3, AsF_5, and F_2 (3:3:1) in a special quartz reaction vessel which made it possible to carry out the synthesis at 77 K. The product is highly pure, and is formed at a rate of more than 1 g h^{-1}. The ultraviolet irradiation of a mixture of CF_3NF_2, AsF_5, and F_2 gives the hexafluoroarsenates of NF_4^+, $N_2F_3^+$, and N_2F^+.[18] $^{15}NF_4AsF_6$ has been obtained photochemically[18] from $^{15}NF_3$, F_2, and AsF_5; the $^{15}NF_3$ required was synthesised from $^{15}N_2$ and F_2 in an electrical glow discharge.[19]

$NF_4^+SbF_6^-$. TFA fluoroantimonate was first obtained by the reaction of NF_3 with F_2 and SbF_5 in hydrogen fluoride.[7,20] When an equimolar mixture of the starting materials was heated in a Monel metal reaction vessel at 473 K and a pressure of up to 185 atm for 2–3 d, more than 40% of the NF_3 added to the autoclave was used up. The product contained up to 25% impurities—metal salts formed by corrosion of the walls of the reaction vessel.

It was also found[7] that the TFA salt can be obtained in the absence of hydrogen fluoride.[3,20] A mixture with $NF_3:SbF_5 \approx 1:1$ with a slight excess of F_2 was placed in a heated Monel metal vessel and kept in it at 373–473 K for several days.[3] The reaction took place comparatively slowly; the degree of transformation of NF_3 after 50 h was 11% at 373 K, and 41% at 473 K. Under these conditions, the product is apparently a mixture of TFA salts containing the SbF_6^- anion and the $Sb_2F_{11}^-$ and $Sb_3F_{16}^-$ polyanions. When the TFA fluoroantimonate specimens are heated for a long time in a vacuum at 473 K, the polyanions decompose to give NF_4SbF_6.[5] Similarly, for example, $O_2^+Sb_2F_{11}^-$ is converted into $O_2^+SbF_6^-$ by heating in a vacuum to a temperature above 403 K.[21]

Further refinements[22] showed that the reaction of NF_3 with F_2 and SbF_5 at 373–397 K and a pressure of ~210 atm gives $NF_4Sb_3F_{16}$, which in a vacuum at 473 K over a period of 2–3 d gives up SbF_5 and is converted into NF_4SbF_6. It was later found[22,23] that the reaction of NF_3 with F_2 and SbF_5 at 388 K with subsequent thermal decomposition of the product in a vacuum at 473 K gives a substance with composition close to $NF_4Sb_2F_{11}$, which is converted into NF_4SbF_6 in a vacuum at a higher temperature (523–533 K). After heating for 1–1.5 h at 523–533 K in a vacuum with removal of the volatile decomposition products, the specimen is completely converted into NF_4SbF_6, and in this time interval not more than 3% of the NF_4SbF_6 obtained decomposes. Appreciable decomposition of the NF_4SbF_6 formed in this operation takes place only at 548–573 K. From these results it was concluded[23] that the reaction of NF_3 with F_2 and SbF_5 at 388–473 K and a pressure of up to 200 atm gives a product $NF_4SbF_6.nSbF_5$, where n = 2.1–3.2, depending on the reaction conditions. Thermal decomposition in a vacuum at 473 K lowers the value of n to 0.8–1.1, and thermal decomposition at 533 K gives pure NF_4SbF_6.

Thus the synthesis of NF_4SbF_6 by heating a mixture of NF_3, F_2, and SbF_5 is fairly laborious and time-consuming, but it can be used to obtain the salt in large quantities. In a simpler version[24] of the "thermal" synthesis of the salt, antimony pentafluoride is replaced by the trifluoride:

$$NF_3 + 2F_2 + SbF_3 \rightarrow NF_4SbF_6 .$$

The process is carried out at 523 K and 30–70 atm over a period of several days, and gives pure NF_4SbF_6 containing no significant quantities of polyfluoroantimonates.

The salt NF_4SbF_6 can be obtained by the reaction of NF_3 with $KrF^+SbF_6^-$ at room temperature, or by the reaction of equimolar quantities of KrF_2, NF_3, and SbF_5 in hydrogen fluoride at 295 K,[25] but this method requires krypton fluoride, which is not readily available. In addition, $NF_4SbF_6.nSbF_5$ is also formed when a mercury lamp is used to irradiate a mixture of SbF_5, NF_3, and F_2 in a quartz vessel at room temperature.[17] The reaction is slow, and the product consists of a mixture of dioxygenyl and TFA fluoroantimonates. The reaction of fluorine with quartz liberates oxygen, which is oxidised to O_2^+ in the presence of fluorine and under the influence of ultraviolet radiation:

$$5F_2 + 2SiO_2 + 4SbF_5 \rightarrow 2SiF_4 + 2O_2^+Sb_2F_{11}^- .$$

TFA fluoroantimonates can apparently also be obtained by a plasmochemical method, for example from SbF_5, NF_3, and F_2 or from SbF_5, N_2, and F_2 using an electrical glow discharge, but the reaction is difficult, because of the low volatility of SbF_5.

$NF_4^+BF_4^-$. Attempts to obtain this salt by analogy with NF_4AsF_6 and NF_4SbF_6, that is by activating the system NF_3 + F_2 + BF_3, appear quite natural, and were probably made during the search for methods for synthesising the salts of TFA with the AsF_6^- and SbF_6^- anions. Thus in 1969, an unsuccessful attempt to synthesise NF_4BF_4 in a glow discharge from NF_3, F_2, and BF_3 at a temperature of the walls of the reaction vessel of 193 K was reported.[26] Instead of the expected compound, the product obtained was $O_2^+BF_4^-$ and other salts, which were hydrolysed with the liberation of oxides of nitrogen. A later paper[27] reported that one of the authors of Ref.8 in 1967 had subjected a mixture of NF_3 with F_2 and BF_3 to an electric discharge, but obtained $N_2F^+BF_4^-$, and not NF_4BF_4. An attempt was made[7] to obtain NF_4BF_4 by the double decomposition of salts of the NF_4^+ cation and salts of the BF_4^- anion (see Ref.27). After NF_4BF_4 was synthesised in 1969[9] from NF_3, F_2, and BF_3 in an electrical glow discharge, it became clear that the authors of Refs.8 and 26 had been very close to success, and had failed because the temperature of the walls of the reaction vessel at which the experiments in the discharge were carried out was not sufficiently low.

The synthesis of NF_4BF_4 is carried out in a quartz discharge tube immersed in liquid nitrogen; a mixture of NF_3 and BF_3 in almost equimolar proportions with a slight excess of NF_3 is first condensed, after which the discharge is switched on and fluorine is slowly introduced into the reaction vessel to maintain a pressure of 30–55 mmHg in it.[9,10,28] When one of the reagents (NF_3 or BF_3) is used up, the pressure begins to increase in the apparatus in proportion to the rate of supply of fluorine; when the supply of fluorine is stopped, the pressure remains constant, indicating that the reaction is complete. The efficiency of this method of synthesis corresponds to tens of grams of product per hour in a reactor volume of 50–100 cm^3.

The photochemical method[17,18] for synthesising NF_4BF_4 has a lower efficiency than the plasmochemical method. The salt is obtained in a yield of less than 1% when a mixture of NF_3 with F_2 and BF_3 is irradiated with ultraviolet light at room temperature.[17] The low-temperature photolysis of mixtures of the same reagents is more efficient;[18] when a high-pressure mercury lamp is used as the source of ultraviolet radiation, a yield of NF_4BF_4 greater than 3 g h^{-1} is achieved. During the photolysis, it is necessary to introduce fresh portions of the reagents into the reaction vessel at intervals, to prevent the formation of a screening layer of the product on the surface of the condensed reagents. The same precautions should also be taken in the plasmochemical preparation of the salt if the process is carried out for a long time.[10,28]

TFA fluoroborate has also been synthesised by the action of bremsstrahlung on a mixture of NF_3 with F_2 and BF_3 (1:6:1) cooled to 77 K; the yield of the product in the reaction vessel with mixing of the contents was over 100 mg h^{-1} for a radiation power of 100 Mrad h^{-1}.[27]

A method for preparing NF_4BF_4 by the action of a laser on a mixture of NF_3 and BF_3 with a different gaseous source of fluorine, namely SF_6, has been patented.[29]

According to data reported in Ref. 22 (see note 3 of Ref. 22), the following method was developed for the synthesis of NF_4BF_4:

$$CsF + HF \rightarrow CsHF_2,\ NF_4SbF_6 + CsHF_2 \rightarrow CsSbF_6 + NF_4HF_2,$$
$$NF_4HF_2 + BF_3 \rightarrow NF_4BF_4 + HF$$

(all the reactions are carried out in HF). The NF_4BF_4 formed is extensively contaminated by $CsSbF_6$, which is removed by treating with bromine pentafluoride; in BrF_5, however, the reaction $NF_4BF_4 + CsSbF_6 \rightarrow CsBF_4 + NF_4SbF_6$ takes place, and the NF_4BF_4 is contaminated with NF_4SbF_6. The replacement of CsF by silver fluoride[30] in this process eliminated the stage involving treatment with bromine pentafluoride, but did not lead to an appreciable increase in the purity of the product. Further improvement[22,31] of this method gave NF_4BF_4 specimens with a purity exceeding 99%. It has been suggested that $CsBF_4$ be used instead of $CsHF_2$, and that the reaction

$$CsBF_4 + NF_4SbF_6 \rightarrow CsSbF_6 + NF_4BF_4$$

be carried out in HF at 195 K in the presence of a 10–15% excess of NF_4SbF_6, which decreases the solubility of $CsSbF_6$ in HF.

The preparation of NF_4BF_4 by the reaction of an equimolar mixture of KrF_2, NF_3, and BF_3 at 295 K in HF has been reported.[25]

Of all the methods examined for the synthesis of NF_4BF_4, the plasmochemical method appears to be the most accessible, simple, and efficient.

$NF_4^+HF_2^-.nHF$. The synthesis of this salt can be regarded as resulting from attempts to prepare TFA fluoride $NF_4^+F^-$, which, if it were stable, would be a unique compound containing 87% active fluorine. An attempt might be made to obtain $NF_4^+F^-$, for example, by a double decomposition of the type

$$NF_4^+SbF_6^- + M^+F^- \rightarrow NF_4^+F^- + MSbF_6.$$

Work by a research group (see note 4 in Ref. 11) showed that the double composition of LiF and NF_4SbF_6 in HF at room temperature gives an $LiSbF_6$ precipitate and a solution containing NF_4^+ cations, but attempts to isolate the TFA salt from the solution were unsuccessful, since the salt decomposed to NF_3, F_2, and HF.

The authors cited[11] used CsF as the ionic fluoride, but it was found that the reaction of NF_4SbF_6 with CsF in HF at 195 K does not give $NF_4^+F^-$, but leads to the formation of the unstable solid compound $NF_4^+HF_2^-.nHF$. For the synthesis of this salt, equimolar quantities of NF_4SbF_6 and CsF are placed in HF, the mixture is kept at room temperature and then cooled to 195 K, and the $CsSbF_6$ precipitate is filtered off. The excess of solvent is removed almost completely by distilling at 228 K; the residue consists of a transparent liquid, which solidifies at 195 K. The compound dissociates at 298 K:

$$NF_4HF_2 \cdot nHF \rightarrow NF_3 + F_2 + (n+1)HF$$

and the molar ratio NF_3:HF is ~10.1 at the start of the decomposition, and 1.54 at the end. It is extremely difficult to remove the solvating HF molecules completely, since the salt decomposes. Solutions of NF_4HF_2 in HF are stable at room temperature, and can be used to synthesise other TFA salts.

$NF_4^+Be_2F_5^-.BeF_2$, prepared by the thermal decomposition of $(NH_4)_2BeF_4$, reacts with a concentrated solution of NF_4HF_2 in HF. The reagents are kept for 65 h at 298 K to give $NF_4.Be_2F_5$, containing ~16% impurities.[32]

$NF_4^+AlF_4^-$. A specimen of NF_4AlF_4 containing ~17% impurities was synthesised by analogy with $NF_4Be_2F_5$, by the reaction of AlF_3 with NF_4HF_2 in HF.[32] The reaction

$$M_3AlF_6 + 3NF_4SbF_6 \rightarrow 3MSbF_6 + (NF_4)_3AlF_6$$

(M = Cs or Na) could not be carried out in BrF_5 at 298 K, or in HF at 195 K, or in molten NF_4SbF_6 at 548 K at an increased pressure of NF_3 and F_2.[32]

$(NF_4^+)_2SiF_6^{2-}$. Attempts to obtain the TFA salt with the SiF_5^- anion by low-temperature photolysis[18] were unsuccessful, as were attempts to synthesise TFA hexafluorosilicate by the double decomposition of NF_4SbF_6 and Cs_2SiF_6 in anhydrous HF.[33] Success was achieved by the reaction of SiF_4 with $NF_4HF_2.nHF$, previously freed (as far as possible) from excess HF:

$$2NF_4HF_2 \cdot nHF + SiF_4 \rightarrow (NF_4)_2SiF_6 + 2(n+1)HF.$$

This reaction gave a 95.5% pure specimen of $(NF_4)_2SiF_6$. The reaction of $(NF_4)_2SiF_6$ with an excess of SiF_4 does not give NF_4SiF_5, in contrast to $(NF_4)_2GeF_6$, which reacts with an excess of GeF_4 to give NF_4GeF_5.[33]

$NF_4^+PF_6^-$. Low-temperature photolysis[18,34] has proved suitable for the synthesis of this salt from a mixture of NF_3, PF_5, and F_2 in the ratio 3:3:1. The rate of formation of the product was only 10 mg h^{-1}. NF_4PF_6 can be obtained in larger quantities by the replacement reaction

$$NF_4BF_4 + PF_5 \rightarrow NF_4PF_6 + BF_3.$$

When a mixture of NF_4BF_4 with an excess of PF_5 is kept for 64 h at 298 K, the NF_4BF_4 is practically completely converted into NF_4PF_6.[18,35] In the reaction of NF_4BF_4 with an excess of PF_5 in HF at room temperature, the conversion of NF_4BF_4 into NF_4PF_6 is only partial (8–17%).[18] The salt can also be obtained by the reaction of NF_3 with KrF_2 and PF_5 (1:1:1) in HF at 295 K.[25]

$NF_4^+SO_3F^-$. This salt is obtained[36] by the double decomposition of NF_4SbF_6 and $CsSO_3F$ in anhydrous HF at room temperature with subsequent cooling to 195 K and filtration

at this temperature; the solvent is removed by distilling at 243 K. Solutions of NF_4SO_3F in HF are stable at 298 K for several days. TFA sulphate cannot be obtained by the analogous reaction of NF_4SbF_6 with Cs_2SO_4, since caesium sulphate reacts with HF to give $CsSO_3F$.

$NF_4^+ClO_4^-$. TFA perchlorate was synthesised[11] by the reaction of equimolar quantities of NF_4SbF_6 and $CsClO_4$ in anhydrous HF. The mixture of reagents is kept for 15 h at 195 K and for 2 h at 228 K, after which the $CsSbF_6$ precipitate is separated at 195 K, and the solvent distilled off. The purity of the product reaches 95%. Attempts to synthesise NF_4BrO_4 and NF_4IO_4 by analogous methods were unsuccessful: $NF_4.BrO_4$ is extremely unstable in HF, and decomposes explosively when isolated from solution, and IO_4^- is readily fluorinated to $IF_4O_2^-$ in HF or BrF_5.

$(NF_4^+)_2TiF_6^{2-}$ and TFA polyfluorotitanates. $(NF_4)_2TiF_6$ was obtained[37] by the reaction of saturated solutions of NF_4SbF_6 and Cs_2TiF_6 in HF (molar ratio $NF_4SbF_6:Cs_2TiF_6 = 2:1$) at room temperature, followed by filtration of the solution at 195 K and distillation of the volatile products at 323 K. Fluorotitanates containing polyanions are formed[37] by displacing BF_3 from NF_4BF_4 using titanium tetrafluoride:

$$NF_4BF_4+nTiF_4\rightarrow NF_4TiF_5\cdot(n-1)TiF_4+BF_3.$$

The reaction of NF_4BF_4 with TiF_4 in anhydrous HF at room temperature gives $NF_4Ti_2F_9$ and $NF_4Ti_3F_{13}$, and the composition of the products depends on the preliminary treatment of the TiF_4 taken for the reaction; if a specimen previously treated with fluorine at 523 K and 70 atm is used, the product is $NF_4Ti_3F_{13}$. The reaction of NF_4BF_4 with TiF_4 without a solvent at 443 K gives $NF_4Ti_2F_9$. Heating TiF_4 with an excess of NF_3 and F_2 at 453–468 K and a pressure of up to ~160 atm gives a product with a composition close to $NF_4Ti_6.F_{25}$:

$$NF_3+F_2+6TiF_4\rightarrow NF_4Ti_6F_{25}.$$

According to Ref. 25, $(NF_4)_2TiF_6$ is formed by the reaction of NF_3 with KrF_2 and TiF_4 (2:2:1) in HF at 295 K; the vibrational spectra of the product given in Ref. 25, however, differ from the spectra of $(NF_4)_2TiF_6$ given in Ref. 37.

$(NF_4^+)_2MnF_6^{2-}$. The fluorination of a mixture of $MnCl_2$ and CsF at 673 K was used to obtain Cs_2MnF_6, which then reacted with NF_4SbF_6.[38] The mixture of Cs_2MnF_6 and NF_4SbF_6 (1:2) in anhydrous HF was kept for 30 min at 298 K, after which the solution was cooled to 195 K. The solvent was then distilled off, to give 91.27% pure $(NF_4)_2MnF_6$. The salts $(NF_4)_3MF_6$ (M = Mn, Co, Cu) could not be synthesised in this way, because of the solvolysis of MF_6^{3-} in HF. The salt $(NF_4)_3CoF_6$ similarly could not be obtained by the reaction of CoF_3 with NF_4HF_2 in HF at 228 K.[38]

$(NF_4^+)_2NiF_6^{2-}$. The double decomposition of Cs_2NiF_6 and NF_4SbF_6 (1:2) in anhydrous HF at 298 K gives $(NF_4)_2.NiF_6$,[39,40] which is separated from $CsSbF_6$ by filtration at 195 K, and freed from solvent by distillation at 298 K.

$NF_4^+GeF_5^-$, $(NF_4^+)_2GeF_6^{2-}$. NF_4GeF_5 was obtained by the low-temperature photolysis[18] of a mixture of NF_3 with GeF_4 and F_2 (3:3:1). The rate of formation of the salt was only 25 mg h^{-1}, so that a different method was proposed[18] for preparing NF_4GeF_5, based on the reaction of NF_4BF_4 with a large excess of GeF_4. At room temperature without a solvent, GeF_4 displaces BF_3 from NF_4BF_4; after 64 h, the degree of conversion of NF_4BF_4 into NF_4GeF_5 was 65%, and complete conversion required repeated treatment of NF_4BF_4 with germanium tetrafluoride. The reaction of NF_4BF_4 with GeF_4 in anhydrous HF at 298 K gives 85% conversion of NF_4BF_4, but the product is a mixture of NF_4GeF_5 and $(NF_4)_2.GeF_6$. Germanium tetrafluoride is a weaker Lewis acid than AsF_5, so that it does not displace AsF_5 from NF_4AsF_6 in HF.

The salt $(NF_4)_2GeF_6$, the first TFA salt to be synthesised with a doubly-charged anion, can be obtained in quantitative yield by keeping NF_4GeF_5 in an excess of HF at 298 K. Treatment of $(NF_4)_2GeF_6$ with a large excess of GeF_4 at 298 K gives NF_4GeF_5 in quantitative yield.[18]

$NF_4^+NbF_6^-$. This compound was obtained[25] by the reaction of KrF_2 with NF_3 and NbF_5 (1:1:1) in anhydrous HF at room temperature.

$NF_4^+SnF_5^-$, $(NF_4^+)_2SnF_6^{2-}$. When mixtures of NF_3 with F_2 and SnF_4 are heated (573 K, ~150 atm), a TFA salt is not formed.[41] $(NF_4)_2SnF_6$ was synthesised from Cs_2SnF_6 and NF_4SbF_6 (1:2) in anhydrous HF at room temperature, followed by filtration of the solution at 193 K.[41] The reaction of equimolar quantities of NF_4BF_4 and SnF_4 in anhydrous HF at 298 K gives practically pure NF_4SnF_5. If however a two-fold excess of NF_4BF_4 is taken, the product is not NF_4SnF_5 but only a small quantity of $(NF_4)_2SnF_6$, even after prolonged reaction.[41]

$NF_4^+XeF_7^-$, $(NF_4^+)_2XeF_8^{2-}$. The reaction of XeF_6 with NF_4HF_2 in HF gives 98% pure NF_4XeF_7.[42,43] Prolonged exposure of a specimen to laser radiation with a wavelength of 4880 Å at room temperature leads to the decomposition of NF_4XeF_7 to give $(NF_4)_2XeF_8$ and XeF_6.

$NF_4^+WF_7^-$. A specimen of NF_4WF_7 containing 1.61% $CsSbF_6$ was synthesised[44] by the reaction of WF_6 with NF_4HF_2.

$NF_4^+WOF_5^-$, $NF_4^+W_2O_2F_9^-$. NF_4WOF_5 was synthesised by the reaction of WOF_4 with a concentrated solution of NF_4HF_2 in HF at 298 K.[45] When heated in a sapphire reaction vessel in a vacuum, NF_4WOF_5 is completely converted into $NF_4W_2O_2F_9$:

$$3NF_4WOF_5\rightarrow 2NF_3+OF_2+WF_6+NF_4W_2O_2F_9.$$

In anhydrous HF, solvolysis of NF_4WOF_5 takes place, again giving $NF_4W_2O_2F_9$.

$NF_4^+BiF_6^-.nBiF_5$. Heating equimolar quantities of NF_4BF_4 and α-BiF_5 at 448–453 K leads to the liberation of BF_3 and the formation of NF_4BiF_6.[23] The same reaction can be carried out at room temperature in anhydrous HF. As in the synthesis of TFA fluoroantimonate, the direct synthesis of TFA fluorobismuthate from NF_3, F_2, and BiF_5 gives salts of polyanions, chiefly $Bi_2F_{11}^-$. Heating a mixture of NF_3 with F_2 and BiF_5 at 448 K and a pressure of 167 atm gives a product having the formula $NF_4BiF_6.0.6BiF_5$. The thermal decomposition of $NF_4BiF_6.nBiF_5$ in a vacuum at 553 K gives $NF_4.BiF_6$.[23] A study[46] of the properties of NF_4BiF_6 as a possible replacement for NF_4SbF_6 in the preparation of TFA salts by double decomposition with alkali metal salts showed that NF_4BiF_6 has no advantages over NF_4SbF_6.

$NF_4^+UF_7^-$. A specimen of NF_4UF_7 containing small quantities of NF_4SbF_6 and $CsSbF_6$ was obtained[44] by the reaction of UF_6 with NF_4HF_2 in 88% yield relative to NF_4HF_2.

$NF_4^+UOF_5^-$. This salt was synthesised[47] from UOF_4 and NF_4HF_2 in anhydrous HF. The possible synthesis of NF_4UOF_5 by the double decomposition of NF_4SbF_6 and the corresponding alkali metal salt is inapplicable in this case, because of

the very low solubility of NF_4UOF_5 in HF. It was also impossible to synthesise the salt from UOF_4, CsF, and NF_4SbF_6 in HF.

Synthesis of other TFA salts. An unsuccessful attempt to prepare NF_4ClOF_4 and NF_4BrOF_4 by the double decomposition of NF_4SbF_6 and the corresponding caesium salts in BrF_5 at room temperature has been described.[11] The reaction of NF_4SbF_6 with $CsBrOF_4$ gives NF_3, fluorine, $BrOF_3$, and $CsSbF_6$, and $CsClOF_4$ reacts with BrF_5 to give $CsBrF_6$ and $ClOF_3$. Anhydrous HF cannot be used as solvent, since it reacts with $CsBrOF_4$. TFA nitrate cannot be obtained by double decomposition in HF, since $CsNO_3$ reacts with HF to give NO_2^+. It was also impossible to carry out F–Cl exchange between NF_4^+ and BCl_3 or between NF_2O^+ and BCl_3 to obtain salts of NCl_4^+ and NCl_2O^+ cations.[11] The double decomposition of $CsIO_2F_4$ and NF_4SbF_6 in HF does not give $NF_4IO_2F_4$, but gives *cis*- and *trans*-OIF_4OF.[11,48] The synthesis of NF_4MF_6, where M = Ru, Rh, Pt, and Au, using KrF_2 has been described[49] (without any experimental details), as has the preparation of NF_4MnF_5, formed in the HF + KrF_2 + MnO_3F + NF_3 (or N_2F_4) system.[50]

The Possible Existence of NF_5

The NF_4^+ cation can be regarded formally as an ion formed by the removal of a fluoride ion from the hypothetical higher fluoride of nitrogen NF_5. The existence of this fluoride as a sufficiently stable compound is unlikely.[12] Nevertheless, the possible existence of a compound with the empirical formula NF_5, for example as the solvated ion pair $NF_4^+F^-$ at low temperatures in an inert medium, cannot be completely excluded.

The formation of a new unstable nitrogen fluoride was noted[51] in a study of the products obtained by the radiolysis of a mixture of NF_3 with F_2 using uranium fission products. Reliable identification of the compounds was practically impossible, since the quantity of substance formed was 1–10 μmole; the authors[51] suggested, however, that they had synthesised NF_5 or F_3NNF_3. The formation of an unstable unidentified nitrogen fluoride was also observed when liquid NF_3 was irradiated at 77 K with electrons with an energy of 800 keV.[52] The formation of small quantities of a white solid substance was observed[27] as a result of the action of bremsstrahlung with a dose of 100 Mrad on a mixture of NF_3 with an excess of fluorine at 77 K. This substance decomposed at 143 K to give NF_3. The condensation of BF_3 into the mixture of the products after irradiation at 77 K, and subsequent heating of this mixture, gave a small quantity of NF_4BF_4, possibly confirming the decomposition

$$NF_4^+F^- + BF_3 \rightarrow NF_4BF_4.$$

The Mechanism of the Reactions Involved in the Synthesis of TFA Salts

A general method for preparing salts of fluorocations involves the action of a fluoride ion acceptor EF_n on a covalent fluoride RF:

$$RF + EF_n \rightarrow R^+[EF_{n+1}]^- \quad (1)$$

where E represents an atom of B, P, V, As, Sb, etc., and R a group such as ONF_2, $OClF_2$, ClF_4, etc. In a number of cases, polyatomic cations made up of non-metal atoms are formed by the action of EF_n on a mixture of two compounds

$$RF + Z + EF_n \rightarrow [RZ]^+[EF_{n+1}]^-$$

where Z = Cl_2, H_2S, etc.[12] Reaction (2), describing the formation of TFA salts, is usually referred to as the direct synthesis of TFA salts:

$$NF_3 + F_2 + EF_n \rightarrow [NF_4]^+[EF_{n+1}]^-. \quad (2)$$

A second route to NF_4^+ cation is based on the oxidation of nitrogen trifluoride, which can be carried out only using an extremely strong oxidising agent, such as a krypton salt:

$$NF_3 + [KrF]^+[EF_{n+1}]^- \rightarrow [NF_4]^+[EF_{n+1}]^- + Kr. \quad (3)$$

Since nitrogen pentafluoride as starting material does not exist, reaction (1) cannot be used to synthesise NF_4^+, and the direct synthesis of the NF_4^+ cation is achieved by the action of heat or other source of energy on the NF_3 + F_2 + EF_n system (reaction (2)). The methods for obtaining TFA salts described above show that the NF_4^+ ion can be synthesised either by heating the starting materials or by plasmochemical, photochemical, or radiation-chemical methods.

The direct synthesis of TFA salts is possible when EF_n is a fairly strong Lewis acid, monomeric, volatile, and stable under the conditions of the reaction. These requirements are completely or partly satisfied by BF_3, PF_5, GeF_4, AsF_5, SbF_5, and BiF_5. The Lewis acid taken for the direct synthesis accepts a fluoride ion and forms a stable anionic fluoro-complex.

The action of a stronger Lewis acid on a TFA salt with an anion formed by a weaker Lewis acid (for example NF_4BF_4) can displace the weaker acid (BF_3) and give a new salt with the fluoro-anion of the stronger acid. This method has been used to obtain salts of TFA and the corresponding anionic fluoro-complexes by the action of PF_5, TiF_4, GeF_4, SnF_4, and BiF_5 on NF_4BF_4. Boron trifluoride can displace HF from NF_4HF_2 to give NF_4BF_4.

The third group of reactions used for the synthesis of TFA salts involves the double decomposition of NF_4SbF_6 and caesium salts in anhydrous HF. The chief requirement of these reactions is that the starting materials should be soluble, and one of the products ($CsSbF_6$) insoluble, in HF; when this condition is satisfied, it is possible to isolate a new TFA salt, which however entrains appreciable quantities of impurity. This method has been used to prepare NF_4HF_2, NF_4SO_3F, NF_4ClO_4, $(NF_4)_2TiF_6$, $(NF_4)_2MnF_6$, $(NF_4)_2NiF_6$, and NF_4SnF_5.

A unique group of reactions for synthesising TFA salts is formed by those based on TFA hydrogen fluoride. The use of this compound is appropriate when double decomposition is impossible because the starting materials are insoluble or react with the solvent, or when the Lewis acid EF_n is polymeric and non-volatile. Salts of TFA with the corresponding anionic fluoro-complexes have been synthesised by the reactions of NF_4HF_2 with BeF_2, AlF_3, SiF_4, XeF_6, WF_6, WOF_4, UF_6, and UOF_4.

NF_4SbF_6, NF_4PF_6, $(NF_4)_2TiF_6$, NF_4NbF_6, and various other TFA salts have been obtained by oxidising nitrogen trifluoride (reaction (3)).

The mechanism of formation of the NF_4^+ cation was first represented as a set of elementary stages, without any firm experimental proof of the possibility of these stages. For the synthesis of NF_4^+ in an electrical discharge, for example, the following scheme was proposed:[8]

$$NF_3^+ + F_2 \rightarrow NF_4^+ + F,\ NF_3^+ + F \rightarrow NF_4^+,\ NF_3 + F_2^+ \rightarrow NF_4^+ + F,$$
$$NF_3 + F^+ \rightarrow NF_4^+.$$

The formation of NF_3^+, F_2^+, and F^+ ions is possible in the plasma of a glow discharge, which is a highly non-equilibrium

system, as a result of the presence of electrons with energies sufficient to ionise NF_3, F_2, or F. This ionisation cannot take place, however, on thermal or photochemical excitation of the reagents. This led[17] to an examination of the possible formation of the AsF_6 radical as an intermediate product of the direct synthesis of NF_4AsF_6. The AsF_6 radical might be formed by the reaction of F atoms with AsF_5 molecules, and, in the opinion of the authors cited,[17] should be a very strong oxidising agent, comparable with PtF_6 and capable of oxidising NF_3:

$$NF_3 + AsF_6 \rightarrow NF_3^+AsF_6^-,\ NF_3^+AsF_6^- + F_2 \rightarrow NF_4^+AsF_6^- + F.$$

This idea of the role of AsF_6 radicals might be extended to the synthesis of other TFA salts, and also dioxygenyl or xenon salts. The possibility of this mechanism for the formation of NF_4^+ was confirmed[30] when EPR recorded both stable pyramidal radical-cations NF_3^+ and unstable radicals AsF_6, SbF_6, and Sb_2E_{11}, produced by the γ-irradiation of specimens of NF_4AsF_6 and $NF_4SbF_6.0.8SbF_5$, cooled to 77 K. The formation of NF_3^+ radical-cations was also observed[53] by EPR in the low-temperature photolysis of NF_3–F_2–AsF_5 and NF_3–F_2–BF_3 mixtures. The EPR spectra of $^{14}NF_3^+$ and $^{15}NF_3^+$ radical-cations, generated by the γ-irradiation of TFA salts or by low-temperature ultraviolet photolysis, have also been studied.[54]

More detailed studies[55] of the thermal decomposition of NF_4BF_4 and NF_4AsF_6 showed, however, that the mechanism for the synthesis of salts based on radicals of the AsF_6 type is inapplicable. EPR was unable to detect any signs of the reaction of F atoms with AsF_5 to give AsF_6 radicals. Moreover, a kinetic study of the thermal decomposition of NF_4BF_4 and NF_4AsF_6 made it possible[55] to exclude from consideration a number of proposed stages in the decomposition or synthesis of these salts, and to conclude that the only scheme describing the formation and decomposition of NF_4AsF_6 and not contradicting any available experimental data must include the following reversible reactions:

$$F_2 \rightleftharpoons 2F$$
$$F + NF_3 \rightleftharpoons NF_4$$
$$NF_4 + AsF_5 \rightleftharpoons NF_3^+AsF_6^-$$
$$NF_3^+AsF_6^- + F \rightleftharpoons NF_4^+AsF_6^-.$$

In the opinion of the authors cited,[55] this scheme is applicable to other TFA salts, except those for which oxidative fluorination of the anion takes place during the decomposition. The scheme does not include reactions involving NF_5, whose existence has not been proved, but it assumes the participation of the NF_4 radical, whose existence also has not been proved experimentally. According to calculations[55] based on a Born–Haber cycle, the stage $F + NF_3 \rightarrow NF_4$ should be thermally neutral, and probably takes place without an activation energy.

The degree of dissociation of fluorine molecules under the conditions of the experiments of Ref. 55 on the synthesis of NF_4SbF_6 from NF_3, F_2, and SbF_5 is $\sim 10^{-7}$. It is difficult to decide whether the fairly low concentration of F atoms can ensure the comparatively high rate of formation of NF_4SbF_6, observed by the authors cited,[55] if account is taken of only the reaction of atomic fluorine with NF_3 and the NF_3^+ salt, without assuming the possibility of reactions involving molecular fluorine. The scheme proposed in Ref. 55 for the synthesis and decomposition of TFA salts apparently requires more detailed examination and further experimental justification.

Monofluoroammonium and Difluoroammonium Salts

Of the three possible mixed-ligand fluoroammonium cations H_nNF_{4-n} (n = 1–3), H_3NF^+ and $H_2NF_2^+$ have been obtained. $H_3NF^+X^-$ were synthesised by the action of strong proton acids HX on alkyl fluorocarbamates:[56,57]

$$NHFCO_2R + 2HX \rightarrow H_3NFX + CO_2 + RX.$$

where R = ethyl or isopropyl, and X = ClO_4^-, $CH_3SO_3^-$, or $CF_3SO_3^-$. Weaker inorganic acids such as hydrochloric acid decompose fluoro-carbamates. The reaction of the acids with $NHFCO_2R$ takes place rapidly at temperatures equal to or slightly above room temperature in a solvent (methylene chloride). The extremely hygroscopic H_3NFClO_4 and $H_3NFSO_3CH_3$ melt and decompose at 373–378 K; they attack glass, and decompose on standing. The less hygroscopic and more stable $H_3NFSO_3CF_3$, which melts with partial decomposition at 437–438 K, does not react with glass, and is soluble in ethers and nitriles.

The difluoroammonium salts $H_2NF_2^+AsF_6^-$ and $H_2NF_2^+SbF_6^-$ were obtained[58] by the usual method for synthesising fluorocations, by the action of EF_5 (E = As, Sb) on difluoroamine and HF in a medium of HF at 195 K. The salts are stable at 223 K, but at room temperature they decompose rapidly to give HF, EF_5, F_2, NF_3, and small quantities of *trans*-N_2F_2. An attempt to obtain fluoroammonium cations by the action of fluorine on the ammonium salt NH_4AsF_6 in HF was unsuccessful.[58] Similarly, adduct formation was not observed in the NF_3 + HF + SbF_5 system.[58]

III. PROPERTIES OF TETRAFLUOROAMMONIUM SALTS

The earliest studies[3,7,8,15] established that TFA compounds are ionic. The tetrahedral structure of the NF_4^+ ion is confirmed by the vibrational and ^{19}F NMR spectra. For the NF_4^+ structure with T_d symmetry, there are four forms of normal vibration: $A_1 + E + 2F_2$. All the vibrations are active in the Raman spectrum, and the A_1 line is polarised; in the infrared spectrum, only the triply degenerate vibrations are active. The laser Raman spectrum of NF_4AsF_6 [16] shows the vibrational wavenumbers of the (NF_4^+) groups at 847 cm^{-1} (ν_1, A_1), 445 cm^{-1} (ν_2, E), 1160 cm^{-1} (ν_3, F_2), and 611 cm^{-1} (ν_4, F_2). Intense absorption at 1159 cm^{-1} (ν_3, F_2) and absorption of medium intensity at 611 cm^{-1} (ν_4, F_2) are observed in the infrared spectrum of NF_4AsF_6.[59] A detailed study[19] of the vibrational spectra of $^{14}NF_4AsF_6$ and comparison with $^{15}NF_4$. .AsF_6 gave for the normal vibrations of $^{14}NF_4^+$ the values ν_1 = 848.2, ν_2 = 443.3, ν_3 = 1158.95, and ν_4 = 611.15 cm^{-1}; for $^{15}NF_4^+$, the same vibrations appear at 848.2, 443.3, 1129.7, and 609.35 cm^{-1}. The force constant of the NF stretches of the NF_4^+ ion (6.15 mdyne $Å^{-1}$) is much greater than the force constants 2.15 mdyne $Å^{-1}$ for FNO or 4.31 mdyne $Å^{-1}$ for NF_3, indicating that the strength of the NF bond in the NF_4^+ ion is unusually high for nitrogen fluorides. The estimated interatomic distance N–F in NF_4^+ is 1.24 Å (1.512 Å for FNO and 1.365 Å for NF_3).[19] The anions of the salts have practically no influence on the vibrational spectra of the NF_4^+ ion. The normal vibrations of NF_4^+, recorded in the spectra of all the salts synthesised, lie in a narrow wavenumber range of ~20 cm^{-1}, and this range is possibly determined not so much by the properties of the salts as by the quality of the experimental spectra.

The ^{19}F NMR spectra of TFA salts show that the fluorine atoms in NF_4^+ are equivalent, and that the ion has tetrahedral symmetry. The spectrum of NF_4AsF_6 (solution in HF, 298 K, 94.6 MHz) contains a triplet of very narrow bands of equal

intensity, corresponding to the NF_4^+ ion, with a chemical shift of -213.5 p.p.m. ($CFCl_3$) and a spin–spin coupling constant of 234 Hz.[59] The band width at half-height does not exceed 10 Hz, indicating that there is no N–F quadrupole coupling. Analogous ^{19}F NMR spectra were obtained for other TFA salts.

TFA tetrafluoroborate has been studied by X-ray electron spectroscopy.[28] The energy of the removal of the 1s electron of the N atom for NF_4BF_4 is 417.3 eV, which is much greater than all known values for nitrogen compounds. The energy of the removal of the 1s electron of the F atom for NF_4^+ (694.4 eV) is also greater than all known values. From these data it follows that the negative charge on the F atoms in NF_4^+ is a minimum, and that the N–F bond is less polar than the C–F or B–F bonds. From an analysis of the intensities of the ν_1 line in the Raman spectrum of NF_4BF_4,[27] it was concluded that the bonds in NF_4^+ are more covalent than those in BF_4^-.

The crystal structures of various low-temperature forms of TFA salts have been determined from the X-ray powder diffraction patterns. The salts have a tetragonal lattice with $Z = 2$. The unit cell parameters and values of the calculated density ρ are given in Table 1. The calculated[18,37,39,41] values of the parameters a and c for the lattices of $(NF_4)_2EF_6$, where E = Ge, Ti, Ni, or Sn, were corrected in Ref.38, and the corrected values are given in Table 1. The density of NF_4AsF_6, measured in a perfluorinated amine, is 2.98 g cm^{-3} at 298 K.[15]

Table 1. Crystallographic data for TFA salts.

Salt	Cell parameters, Å		ρ, g cm^{-3}	Refs.
	a	c		
NF_4BF_4	7.01	5.22	2.29	[27]
NF_4BF_4	9.944	5.229	2.27*	[18]
NF_4PF_6	7.577	5.653	2.41	[18]
NF_4AsF_6	7.70	5.73	2.72	[15]
NF_4SbF_6	7.903	5.806	2.98	[23]
NF_4BiF_6	8.006	5.821	3.68	[23]
$(NF_4)_2TiF_6$	6.99	9.28	2.51	[38]
$(NF_4)_2MnF_6$	6.90	9.23	2.64	[38]
$(NF_4)_2NiF_6$	6.828	9.270	2.71	[60]
$(NF_4)_2GeF_6$	6.92	9.25	2.75	[38]
$(NF_4)_2SnF_6$	7.05	9.41	2.93	[38]

* $Z = 4$.

Crystallographic studies[60] of powders and single crystals of 98.9% pure $(NF_4)_2NiF_6$ showed that the compound has a body-centred tetragonal cell, space group $I4/m$. The salt is made up of octahedral NiF_6^{2-} ions and tetrahedral NF_4^+ cations, and has the antifluorite structure. The calculated interatomic distance N–F in the NF_4^+ tetrahedra is 1.30–1.40 Å, and the F...F distance is ~2.2 Å.[60]

TFA salts are colourless crystalline substances, except for the bright-red compound $(NF_4)_2NiF_6$ and the yellow compounds $(NF_4)_2MnF_6$, NF_4XeF_7, NF_4UF_7, and NF_4UOF_5. The salts do not sublime, and almost all decompose without melting. The melting points are ~591 K for NF_4SbF_6 and 614 K for NF_4BiF_6; $NF_4Sb_2F_{11}$ melts at 451 K, and the melt solidifies at 434 K. The melting point of $NF_4HF_2.nHF$ increases with decrease in the number of solvating HF molecules, and approaches room temperature as $n \to 0$.

TFA salts are soluble to different extents in anhydrous HF; the solubility of $(NF_4)_2MnF_6$ is greater than 1.30 g per g HF at 297 K, the solubilities of NF_4SbF_6 and NF_4BiF_6 are 259 mg and 173 mg per g HF at 195 K, and NF_4UOF_5 is sparingly soluble. Bromine pentafluoride, in which TFA salts are less soluble than in HF, can also be used as solvent. The salts are extremely hygroscopic, and react vigorously with water, and also with common organic solvents.

1. The Thermal and Thermochemical Properties of TFA Salts

TFA salts have an unusually high thermal stability. Although the stability of the fluoroantimonate and fluoroarsenate might have been predicted by analogy with other salts of fluoro-cations, the existence of the extremely stable tetrafluoroborate was completely unexpected. The synthesis of each new TFA salt was naturally followed by a study of its thermal stability. Unfortunately, the published results are not standardised, and the data must be regarded as only approximate, particularly because of the strong catalytic influence of the walls and impurities present in the salts on the rate of decomposition. Table 2 gives the temperatures of the start of the decomposition of various TFA salts, recorded by DTA or DSC, and also manometrically or by visual observation of the behaviour of the substance when heated in a sealed capillary. Although these values are understandably inaccurate, they are useful for estimating the relative stability of the salts.

Table 2. Temperatures of the start of the decomposition of TFA salts (T, K).

Salt	T	Salt	T
NF_4BF_4	513	$(NF_4)_2SiF_6$	363
NF_4GeF_5	522*	$(NF_4)_2TiF_6$	473
NF_4SnF_5	543	$(NF_4)_2MnF_6$	373
NF_4PF_6	518*	$(NF_4)_2NiF_6$	383
NF_4AsF_6	543	$(NF_4)_2GeF_6$	511*
NF_4SbF_6	>573	$(NF_4)_2SnF_6$	513
NF_4XeF_7	348	NF_4SO_3F	283
NF_4WF_7	>398**	NF_4ClO_4	273
NF_4UF_7	>398**	NF_4WOF_5	358
		NF_4UOF_5	333

*Temperature of the start of rapid decomposition.
**In a vacuum.

The salt NF_4HF_2 is stable in HF up to room temperature, and decomposes rapidly at 328 K; $NF_4Sb_2F_{11}$ at 523–533 K in a vacuum gives up SbF_5 and is converted into NF_4SbF_6;[23] the salt NF_4BiF_6 is apparently the most stable, and melts at ~614 K.[23] Table 2 shows that the stability of the salts depends markedly on the nature of the anions. Salts with oxygen-containing anions decompose at temperatures below 373 K, whereas salts with the anionic fluoro-complex BF_4^- and anions of the type EF_{n+1}^- ($n = 4$–6) or EF_6^{2-} are much more stable, and even the salt of the weak Lewis acid SiF_4 is stable up to ~363 K. According to recent data[61] obtained by DSC, the decomposition of NF_4BF_4, NF_4PF_6, NF_4AsF_6, NF_4SbF_6, NF_4GeF_5, and $(NF_4)_2GeF_6$ begins at 435, 446, 518, 578, 374, and 440 K respectively, and the maxima of the effects are observed at 530, 533, 596, 655, 475, and 481 K. For NF_4GeF_5, the temperature of the start of the decomposition (374 K) was taken as the temperature of the transformation of the salt into $(NF_4)_2GeF_6$ according to the scheme

$$2NF_4GeF_5 \rightarrow (NF_4)_2GeF_6 + GeF_4$$

and the maximum of the effect (475 K) corresponds to the decomposition stage

$$(NF_4)_2GeF_6 \rightarrow 2NF_3 + 2F_2 + GeF_4 .$$

According to Ref.38, a specimen of $(NF_4)_2NiF_6$ after 6 h at 373 K decomposes to the extent of 9%, but in Ref.62 it is stated that the temperature of the start of the decomposition of this salt is 407 K. The decomposition of $(NF_4)_2MnF_6$ at 373 K for 20 min takes place with acceleration, after which the pressure of the gaseous decomposition products increases linearly.[38] At 373 K after 17 h, 0.17% of the $(NF_4)_2MnF_6$ taken decomposes, whereas at 403 K after the same time interval the degree of decomposition is 0.66%. In a vacuum, NF_4XeF_7 decomposes at rates of 1.6% and 28% per hour at 348 K and 373 K; NF_4WF_7 at 418 K in a vacuum after 1 h decomposes to the extent of 1.4%, and NF_4UF_7 to the extent of 25%.[44] At 358 K, NF_4WOF_5 decomposes at a rate of ~0.03% per hour, and at 428 K after 6.5 h the degree of conversion into $NF_4W_2O_2F_9$ is 90%.[45]

The decomposition of TFA salts with the anions EF_{n+1}^- (n = 3–6) and EF_6^{2-} gives NF_3, F_2, and the corresponding fluorides EF_n, for example $NF_4BF_4 \rightarrow NF_3 + F_2 + BF_3$. The decomposition of $(NF_4)_2NiF_6$ gives non-stoichiometric nickel fluoride, and is described by the equation $(NF_4)_2NiF_6 \rightarrow 2NF_3 + (3 - x/2)F_2 + NiF_{2+x}$. The decomposition of $(NF_4)_2MnF_6$ gives MnF_3 according to the scheme: $2(NF_4)_2MnF_6 \rightarrow 4NF_3 + 5F_2 + 2MnF_3$.

The decomposition of salts with oxygen-containing anions is accompanied by the reaction of fluorine with the anions to give a different set of decomposition products. The decomposition of NF_4UOF_5 is described by the equations $NF_4UOF_5 \rightarrow NF_3 + F_2 + UOF_4$, $2UOF_4 \rightarrow UF_6 + UO_2F_2$; the decomposition products contain a mixture of UOF_4 and UO_2F_2, and the decomposition of NF_4UOF_5 gives OF_2 (in small quantities). At 453 K in a vacuum, NF_4WOF_5 is converted into the more stable $NF_4W_2O_2F_9$ according to the scheme: $3\,NF_4WOF_5 \rightarrow 2NF_3 + OF_2 + WF_6 + NF_4W_2O_2F_9$. The thermal decomposition of NF_4ClO_4 and NF_4SO_3F provides a new method for synthesising the corresponding hypofluorites: $NF_4ClO_4 \rightarrow NF_3 + FOClO_3$, $NF_4SO_3F \rightarrow NF_3 + FOSO_2F$. The decomposition of NF_4ClO_4 can be used to obtain very pure $FOClO_3$, which does not decompose when handled.[63] The hypofluorite $FOIOF_4$ has been obtained[48] as a mixture of *cis*- and *trans*-isomers by the thermal decomposition of the compound $NF_4IO_2F_4$, formed as an intermediate product of the reaction of $CsIO_2F_4$ with NF_4SbF_6 in HF.

The first paper devoted to the study of the kinetics of the thermal decomposition of TFA salts[64] described the decomposition of NF_4AsF_6 specimens in a Monel metal vessel. The specimens were synthesised from NF_3, F_2, and AsF_5 in an electrical glow discharge by the method described in Ref.15. It was found that the dependence of the total pressure p of the gaseous decomposition products of NF_4AsF_6 on time t in the temperature range 448–495 K is given by the equation $p^{3/2} = At + B$, where A and B are coefficients. It was suggested that the decomposition of the salt is described by the equations $NF_4AsF_6 \rightleftharpoons NF_5 + AsF_5$, $NF_5 \rightarrow NF_3 + F_2$, but it was impossible to isolate the suggested intermediate product NF_5 in an Ne matrix to record its infrared spectrum.

The results of Ref.64 appear doubtful, since the decomposition of the salt was studied at 448–495 K, whereas DTA indicates that decomposition begins at a higher temperature, for example ~543 K;[8] this lack of agreement was noted in Ref.12. The authors cited[64] apparently used NF_4AsF_6 specimens containing considerable quantities of impurities; moreover, the walls of the Monel metal vessel react with Lewis acids in the presence of fluorine at high temperatures, so that these vessels are unsuitable for kinetic studies.

The kinetics of the thermal decomposition of NF_4BF_4 and NF_4AsF_6 have been studied[55] in a vessel of synthetic sapphire, which is stable to mixtures of F_2 with BF_3 or AsF_5. The decomposition of NF_4AsF_6 was studied at 473–511 K, and that of NF_4BF_4 at 455–488 K. The time dependence of the total pressure of the decomposition products of the salts obeyed a law analogous to that in Ref.64, but the decomposition was much slower than in Ref.64. A special experiment with a small quantity of NF_4BF_4 at 526 K showed that the decomposition is not autocatalytic, and the linear dependence of $p^{3/2}$ on t is preserved as far as a degree of decomposition of the salt of ~25%. The addition of helium to the system has practically no influence on the rate of decomposition of the salts, the addition of fluorine and NF_3 decreases the rate slightly, and the addition of BF_3 to NF_4BF_4 or of AsF_5 to NF_4AsF_6 leads to a marked decrease in the rate of decomposition.

The decomposition of the salts is characterised by fairly high activation energies: 36.6 ± 0.8 kcal mole^{-1} for NF_4BF_4, and 44.7 ± 4.2 kcal mole^{-1} for NF_4AsF_6.[55] Preliminary studies[39] of the thermal decomposition of $(NF_4)_2NiF_6$ in the range 353–401 K showed that the decomposition of this salt is not autocatalytic, and takes place with an activation energy of 35.161 kcal mole^{-1}. The decomposition of $(NF_4)_2SiF_6$ in the temperature range 361.5–372.5 K has an activation energy of 26.6 kcal mole^{-1}.[33]

Phase transformations have been detected for various TFA salts: for NF_4BF_4 at 493–503 K[10] or at 507 K[18] or at 509 K;[27] for NF_4PF_6 at 398 K;[18] for NF_4AsF_6 at 406 K;[18] and for NF_4GeF_5 at 402 K.[18] The results of a DSC study of various salts, obtained in Ref.61, are given in Table 3. In $NF_4.SbF_6$, the phase transformation almost coincides with the start of the decomposition, and cannot be recorded accurately; the estimated temperature of the start of the transformation is 598 K.[61]

Table 3. Phase transformations in TFA salts.

Salt	Temperature of the start of the effect, K	Temperature of the maximum of the effect, K	ΔH, kJ mole^{-1}	ΔS, J mole^{-1} K^{-1}
NF_4BF_4	497	510	7.58	15.27
NF_4PF_6	404	415	5.90	14.50
NF_4AsF_6	418	428	4.62	10.96

The X-ray powder diffraction pattern of the high-temperature form of NF_4AsF_6, obtained in Ref.61, shows that at 439 K the salt has a cubic lattice with parameter 9.13 Å. For one of the NF_4SbF_6 specimens, a cubic lattice with a = 5.66 Å was found at room temperature.[61]

Until recently, there were no published data on the thermodynamic characteristics of TFA salts. By 1979, the only data were for NF_4BF_4, for which the enthalpy of decomposition had been used to determine experimentally the standard enthalpy of formation, equal to −337.4 kcal mole^{-1} (unpublished data, see Refs.27, 55, and 61), from which it follows that the enthalpy of the reaction $F_2(gas) + NF_3(gas) + BF_3(gas) \rightarrow NF_4^+BF_4^-(solid)$ is −34.6 kcal mole^{-1}.[55] From the estimate in Ref.55, $\Delta H_f^0(NF_4AsF_6) \cong -372$ kcal mole^{-1}. In a DSC study of the thermal decomposition of $(NF_4)_2NiF_6$ and NF_4SbF_6, the values −247 kcal mole^{-1} and −393 kcal mole^{-1} respectively were obtained for the standard enthalpies of formation of these salts.[62] The enthalpy of formation of $(NF_4)_2NiF_6$ had previously[39] been estimated as ~−230 kcal mole^{-1}.

DSC and measurement of the heats of hydrolysis of various TFA salts by water and various aqueous solutions were used[61] to find the enthalpies of formation of the salts. The follow-

ing values of ΔH_f^0 (kJ mole^{-1}) for the solid salts were recommended:

NF_4BF_4	-1410 ± 5	NF_4SbF_6	-1669 ± 12
NF_4AsF_6	-1538 ± 11	NF_4PF_6	-1841 ± 7
NF_4GeF_5	-1473 ± 1	$(NF_4)_2GeF_6$	-1606 ± 5

The affinity of NF_3 for the F^+ ion was estimated as -845 kJ mole^{-1}, and the enthalpy of formation of NF_4^+(gas) as 784 kJ mole^{-1}.[61] From the estimate in Ref. 27, the enthalpy of formation of NF_4^+(gas) is 204 kcal mole^{-1} (853 kJ mole^{-1}). Examination of a Born–Haber cycle with the assumption that the crystal lattice energy of $NF_4^+F^-$ is -630 kJ mole^{-1} gave for the enthalpy of the reaction NF_3(gas) + F_2(gas) → $NF_4^+F^-$ (solid) the value 36 ± 40 kJ mole^{-1}.[61] From a comparison of the enthalpies of formation of TFA salts and other fluorine–nitrogen compounds, it was suggested[65] that the formation of $NF_4^+F^-$ may be exothermic.

2. The Chemical Properties of TFA Salts

TFA salts, like the salts of other fluoro-cations,[12] have an extremely high chemical activity. They react vigorously with water, alcohols, hydrocarbons, and other organic compounds, but in the absence of moisture they can be kept for a long time in Teflon, steel, or quartz containers; they are not sensitive to shock if they are not in contact with a substance capable of being oxidised.

Hydrolysis of the salts leads to the quantitative liberation of NF_3, which is extremely stable to hydrolysis and practically insoluble in water. Measurement of the quantity of NF_3 liberated has been made the basis of a method of elemental analysis which has been used repeatedly in all studies of the synthesis of TFA salts. To avoid a vigorous reaction, several millilitres of water are condensed at 77 K into a vessel containing a specimen of the salt with a mass of 0.5–1.0 g, after which the contents of the vessel are slowly heated to room temperature. The gaseous hydrolysis products are either separated by fractional condensation or analysed chromatographically.[56] The quantitative liberation of oxygen in the molar ratio $NF_3:O_2 = 2:1$ when TFA salts are hydrolysed apparently takes place only for NF_4AsF_6.[61] In the hydrolysis of, for example, NF_4SbF_6, 0.45 mole of O_2 is liberated per mole of NF_3.[23] The decrease in the quantity of oxygen liberated is due to the formation of hydrogen peroxide:

$$NF_4^+ + OH^- \rightarrow NF_3 + HOF,\ 2HOF \rightarrow 2HF + O_2,\ HOF + H_2O \rightarrow HF + H_2O_2$$

The ratio $H_2O_2:O_2$ can vary from one experiment to another, depending on the conditions. A different picture is observed in the hydrolysis of NF_4BiF_6, where 0.86 mole O_2 is liberated per mole of NF_3.[21] The BiF_6^- anion oxidises water according to the equation:

$$BiF_6^- + H_2O \rightarrow BiF_3 + HF_2^- + HF + {}^1/_2O_2$$

and this reaction may also be accompanied by the formation of H_2O_2.

The salt $(NF_4)_2NiF_6$ represents a combination of a fluoro-cation with a fluoro-anion, both of which are strong oxidising agents. The neutral compound NiF_4 corresponding to the NiF_6^{2-} anion is unstable, and decomposes to lower fluorides of nickel with the liberation of fluorine. The hydrolysis of the salt is described approximately by the equation

$$2(NF_4)_2NiF_6 + 5H_2O \rightarrow 4NF_3 + 10HF + 2O_2 + OF_2 + 2NiF_2$$

and the ratio $O_2:OF_2$ varies from one experiment to another. An interesting feature is that OF_2 is formed only when NF_4^+ and NiF_6^{2-} are present together, and is not observed in the hydrolysis of NF_4^+ or NiF_6^{2-} taken separately.[39] The appearance of OF_2 in the hydrolysis products may be due to the fluorination of the intermediate product HOF by the NiF_6^{2-} anion:

$$NF_4^+ + 2H_2O \rightarrow HOF + H_3O^+ + NF_3$$
$$HOF + NiF_6^{2-} \rightarrow OF_2 + HF + NiF_4^{2-}$$

In addition to hydrogen peroxide, ozone in quantities of several mole % is always formed as a side product in the hydrolysis of TFA salts by water, even when the hydrolysis is carried out very carefully.[61]

X-Ray electron spectroscopy has detected the formation of ONF_2^+ and NO_3^- in the reaction of NF_4BF_4 with atmospheric moisture:[28]

$$NF_4^+ + H_2O \rightarrow ONF_2^+ + 2HF$$
$$ONF_2^+ + 3H_2O \rightarrow HNO_3 + 2HF + H_3O^+$$

Up to the present, research workers have been interested chiefly in developing methods for the synthesis of TFA salts, so that a fairly large number of these compounds has been obtained. Subsequent studies will probably be directed towards the investigation of the chemical properties of the salts. TFA salts have a fairly high thermal stability, contain a large quantity of active fluorine, and decompose with the liberation of fluorine over a wide temperature range, and their reactions can be carried out at a controlled rate. These features make it possible to regard TFA salts as promising fluorinating agents in inorganic and organic synthesis. Unfortunately, reactions involving TFA salts have been little studied up to the present.

An early study[67] showed that NF_4SbF_6 in HF fluorinates chlorine to give ClF_3 at room temperature. The thermal decomposition of TFA salts with oxygen-containing cations can be used to synthesise hypofluorites.[36,48,63] The reaction of TeF_5OH with NF_4HF_2 at 250 K gives the stable hypofluorite $FOTeF_5$, whose possible existence was previously doubted.[68]

The reactions of NF_4BF_4 with various aromatic compounds have been studied.[69] The choice of NF_4BF_4 as fluorinating agent is determined, in particular, by the fact that its decomposition products NF_3 and BF_3 are inert towards organic compounds at low temperatures. The reactions of NF_4BF_4 take place by an electrophilic substitution mechanism. Benzene, toluene, and nitrobenzene react rapidly with NF_4BF_4 in anhydrous HF at 273 K to give fluoro-substituted derivatives. In the rapid stage, up to four hydrogen atoms are replaced, and the methyl group of toluene is not fluorinated. After the stage involving the rapid replacement of hydrogen atoms, a much slower stage involving the addition of fluorine atoms at the aromatic bonds begins. The reaction of NF_4BF_4 with hexafluorobenzene at 298 K in HF gives C_6F_8 (yield 94%), in which the added F atoms are in the *para*-position to one another.

3. Application of TFA Salts

TFA salts are solid sources of so-called "available fluorine", which is liberated as F_2 and NF_3 on thermal decomposition. The term "available fluorine" is preferable to the term "active fluorine", since the latter refers only to F_2, and not to fluorine in NF_3. Of the TFA compounds known at present, the following have the highest concentrations of available fluorine (%):

$(NF_4)_2XeF_8$	65.6	NF_4XeF_7	59.0
$(NF_4)_2NiF_6$	64.6	$(NF_4)_2TiF_6$	55.6
$(NF_4)_2MnF_6$	59.9	NF_4BF_4	53.7
$(NF_4)_2SiF_6$	59.0		

In the thermal decomposition of 1 cm^3 of solid $(NF_4)_2NiF_6$, the quantity of available fluorine formed is 12% greater than that from the same quantity of liquid fluorine at 86 K.[39] It is only for NF_4XeF_7 and $(NF_4)_2XeF_8$, however, that complete utilisation of the fluorine present is possible; in other cases, some of the fluorine after the decomposition of the salt remains firmly bound to the element present in the anion.

TFA salts have attracted attention as possible components of solid rocket fuels[70] and gas generators for chemical HF–DF lasers.[23,71,72] The high-density fuel mass[70] contains 25–70% TFA salt, 5–50% high-molecular-weight polytetrafluoroethylene, and 10–25% low-molecular-weight polytetrafluoroethylene. The mixture of these components is dispersed in a suitable fluorinated solvent, after which the solvent is removed and the homogenised mass is pressed or extruded.

The operation of the gas generator[23,73] is based on the liberation of F_2 and NF_3 on the combustion of granules containing a TFA salt with a small quantity of fuel, such as Teflon powder. The heat liberated by the combustion of the Teflon brings about the thermal decomposition of the TFA salt and the dissociation of NF_3 to F atoms and F_2 molecules. The decomposition of TFA salts with anionic fluoro-complexes based on volatile and completely or partly monomeric Lewis acids leads to the liberation of these acids into the gas phase, and hence to contamination of the generated mixture. The liberation of the Lewis acid into the gas phase can be prevented by introducing into the mixture a strong Lewis base such as KF, to bind the acid in a complex; the presence of KF, however, leads to a deterioration in the properties of the mixture. An alternative solution to this problem is to create self-sintering compositions. $(NF_4)_2SnF_6$, which on decomposition gives non-volatile polymeric SnF_4,[41,74] and also $N_2F_3SnF_5$,[75] have been proposed as a basis for these mixtures. TFA salts have also been proposed for increasing the detonation pressure of organic explosives.[76]

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The Possibilities of the Mass-spectrometric Analysis of Involatile and Thermally Unstable Bio-organic Compounds

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The possibilities of the mass-spectrometry of thermally unstable highly polar and organic and bio-organic compounds, based on the direct (without preliminary evaporation) formation of ions of the test compound, are examined.
The bibliography includes 260 references.

CONTENTS

I. Introduction 437
II. Secondary emission ionisation 438
III. Plasma desorption by ^{252}Cf fission fragments 444
IV. Laser desorption 445
V. The mechanisms of ion formation 446

I. INTRODUCTION

The development of modern organoelemental and bio-organic chemistry has led to the need to determine the compositions and structures of highly polar, involatile and thermally unstable compounds, which can be studied by traditional mass-spectrometric methods.

The development of "mild" methods for the ionisation of organic compounds, namely chemical ionisation (Field and Manson,[1] 1968), field ionisation, and field desorption (Beckey,[2] 1969) began in the 1960's and techniques on a wide scale in the 1970's. The mass spectra obtained by these procedures contain intense peaks due to molecular and quasi-molecular ions, but the transfer of the test molecules to the gas phase by heat treatment was not required only in the field desorption method. The field desorption method is therefore used successfully for the analysis of involatile compounds. The advances achieved with the aid of this method have been surveyed in several reviews.[2-5]

During the last decade communications have been published on new methods for the determination of the mass spectra of involatile and thermally unstable compounds (TUC), in which the vaporisation of the test substances before ionisation has been eliminated. These ionisation procedures can be divided into two groups: the methods for the generation of ions from the solid state without heating the specimen and the methods from the selective removal of ions from a solution containing the test compound at room temperature.

The first group comprises methods based on secondary ion emission (SIE) induced by bombarding the test specimen with a beam of primary ions (secondary ion–ion emission) or a beam of neutral atoms (atom–ion emission), the method based on plasma desorption by ^{252}Cf fission fragments, and ionisation by laser radiation (LD).

The second group of methods, which began to develop somewhat later, includes the electrohydrodynamic ionisation method,[6-8] the method based on the field of evaporation of ions from solutions,[9,10] including solutions in involatile solvents deposited on the surface of field desorption emitters,[11] the "electro-scattering" method,[12-16] the "mist formation" method,[17-19] and the method based on the extraction of ions from solutions at atmospheric pressure.[20] Heat treatment of the test substances has been eliminated from all these methods and the latter make it possible to determine the mass spectra of highly polar and involatile thermally unstable compounds without their preliminary chemical modification; the high content of quasi-molecular and in most cases of intense fragment ions ensures that the molecular weights and structures of the test molecules can be determined.

The volatility and in many cases also the stability of the compound diminish with increase of its molecular weight and the scope of a method can be characterised by the upper limit to the mass of the ions obtained with its aid. Towards the middle of 1982, major advances had been achieved by investigators using the methods based on the atom–ion emission in liquid matrices (see below) and plasma desorption by ^{252}Cf fission fragments. Quasi-molecular ions of the unprotected peptide glucagon (a pancreatic hormone), the molecular weight of one of the isotopes of which is 3481.6,[21] and a biological product (bovine insulin) with a molecular weight (MW) of 5729.6 [22] were obtained by the first procedure. A record success was achieved with the aid of the method based on the plasma desorption by ^{252}Cf fission fragments, which yielded the mass-spectrum of an oligonucleotide with a molecular weight of 6278.[23] The absence of the need for enzymic and chemical treatment made it possible to reduce the size of the sample required for the analysis by the new methods and at the same time gave rise to the possibility of identifying compounds present in unpurified biological preparations. Thus the determination of the molecular weight of a peptide by the atom–ion emission method now requires 0.1 nmol of the test substance, while the determination of the aminoacid sequence in it requires 2–50 nmol.[24]

The aim of the present review is to assess the possibilities of those of the above methods which have now found extensive practical applications in the mass-spectrometric analysis of thermally unstable compounds. These include secondary emission ionisation, plasma desorption by ^{252}Cf fission fragments, and laser desorption. The review does not deal with the studies in which the mass spectra of TUC are obtained by traditional ionisation methods—electron impact or chemical ionisation but with updated types of heating or procedures for the introduction of the specimen into the ion formation region, which reduce the degree of thermal decomposition of the product.[25-28] For the analysis of biomolecules, this procedure is not likely to be useful, since an increase in

the molecular weight and in the polarity of the test molecules leads to the requirement for stronger heating and the fraction of quasi-molecular ions in the mass spectrum sharply diminishes or the ions disappear altogether.[26]

II. SECONDARY EMISSION IONISATION

1. Secondary Ion Ionic Emission

When a primary ion beam impinges against a surface, positive and negative ions derived from the adsorbed layers and the material of the support are always present among the secondary particles leaving the surface. The yield of these ions depends on many factors.[29–33] The most important characteristics, which determine quantitatively the ion formation process, are two parameters: the secondary ion emission coefficient $S^{\pm}$ (the parameter $S^{\pm}$ has been called[34,35] the absolute yield of secondary ions), i.e. the number of ions $A^{\pm}$ leaving the surface following the impact by one primary particle, and the ionisation efficiency, i.e. the ratio of the number of dislodged ions to the number of neutral particles which have left the surface.

Impact by the primary ions alters the state of the surface layer. Calculation has shown that at a current of 1×10^{-8} A cm^{-2} the number of ions incident on the surface is 6×10^{-6} ions s^{-1} $Å^{-2}$. Assuming that the energy of a single ion is transmitted to a zone with a radius of 10 Å, we find that such a surface element is exposed to impact after every 8 min. This time is longer by several orders of magnitude than that required to dissipate the energy of the nucleus. For higher current densities of the primary beam, the layers adsorbed on the support are rapidly worn away, which is manifested by a change in the intensity and composition of the ions in the secondary beam.

Benninghoven[34] introduced the concept of the "dynamic" and "static" ion formation regimes under the conditions of secondary ion–ion emission (SIIE). Bombardment of the surface by the primary beam at a current density not exceeding 1×10^{-8} A cm^{-2} has been called the static model; in this case the disruption of the surface layer is insignificant. A method employing the static regime for the preparation of the ions of an organic substance deposited in the support has been called "organic"[36] or molecular[37] SIIE. It has been shown experimentally that irradiation of a thin layer of an organic product deposited on a metallic support by a beam of Ar^+ ions at a current density of 4×10^{-9} A cm^{-2} can give rise to a steady emission of quasi-molecular ions $(M-H)^-$ for several minutes.[38] The ionisation regimes achieved at primary beam current densities exceeding 10^{-8} A cm^{-2} have been called dynamic and are used mostly for the layer-by-layer analysis of metals and semiconductors. The first secondary-emission-mass spectra of organic substances were obtained in 1971 by Tantsyrev and Nikolaev.[39]

In 1976 Benninghoven and co-workers published the secondary-emission mass spectra of four aminoacids (alanine, phenylalanine, cystine, and arginine)[38] and a year later of a further 19 aminoacids and other biologically active compounds (short peptides, vitamins, sulphamide preparations, etc.).[40–42] The spectra of pyrimidine and purine bases, nucleotides and nucleosides,[43] and folid acid[44] were published by the same workers in subsequent years. Bombardment of a specimen in the form of a thin film on a silver support was carried out in the static regime by a primary beam of Ar^+ ions with an energy of 2.25–3.00 keV and at a current density of 4×10^{-9} A cm^{-2} and above. The spectra contained fairly intense peaks due to the ions $(M+H)^+$ and $(M-H)^-$ together with characteristic fragment ions. Stable emission persisted for several minutes but came to a rapid stop if the regime ceased to be static. Subsequently direct evidence was obtained by the method of electronic spectroscopy for chemical analysis (ESCA) that irradiation by a more powerful primary beam entails the disruption of the surface layer of the organic species.[45]

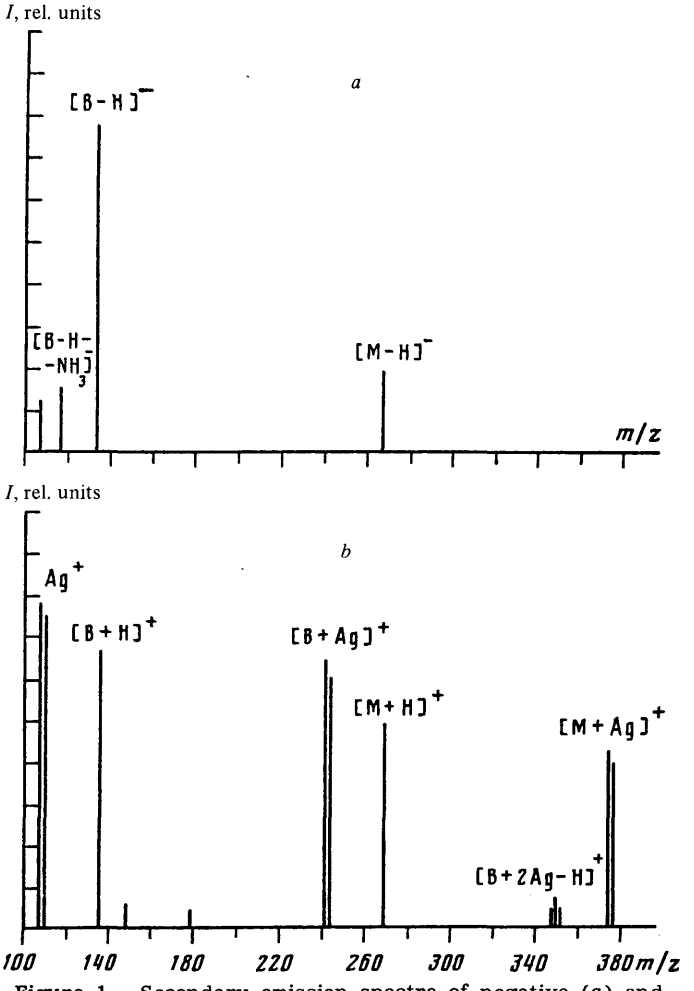


Figure 1. Secondary emission spectra of negative (*a*) and positive (*b*) adenosine ions.[43]

Apart from the protonated molecular and fragment ions of the test substance, the following can appear in secondary-emission mass spectra: (1) cationised molecular ions $(M+Ct)^+$, where Ct^+ is the cation of an alkaline metal or the metal of the support; (2) the intrinsic cations Ct^+ (or anions X^- in the spectra of the negative ions); (3) cluster ions of the type $(M_n + Ct)^+$, $(M_n + H)^+$, and $Ct.(Ct_n + X)^+$; (4) ions of the type $C_mH_n^+$ giving rise to a background spectrum in the region of low masses subsequently referred to as "chemical noise".[46] The spectra of certain compounds also contain clusters $(M - H + 2Ct)^+$ and molecular radical-ions $M^{\pm}$ and $M^{\mp}$. Clusters appear in the spectra of compounds having an

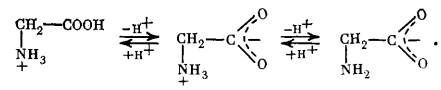
"acid" hydrogen atom,[43,47] while the source of the radical-ions has not been established. Presumably they arise at the phase interface by the interaction of neutral molecules of the test compound with the secondary electrons dislodged from the surface. Radical-ions and their fragmentation products have been observed in the spectra of atropine and nicotinamide.[41,42]

The fragmentation of the $(M + H)^+$ ions has been thoroughly investigated and takes place in accordance with the rules governing the decomposition of even-electron ions.[48,49] For example, the characteristic fragment for aminoacids is $(M - 45)^+$ [38,40-42,50] formed via the reaction

$$R{-}\underset{\overset{|}{\overset{+}{N}H_3}}{CH}{-}COOH \xrightarrow[-CO;\ -H_2O]{} R{-}\overset{+}{C}H{-}NH_2 .$$

The spectra of the purine and pyrimidine bases contain, apart from the intense peaks due to the ions $(M + H)^+$, $(M - H)^+$, or $(M + Ct)^+$, also the peaks due to the $(M + H - NH_3)^+$ and $(M + H - 43)^+$ fragments. In the spectra of the simplest nucleotides and nucleosides the peaks of the ions derived from the bases (B) and formed as a result of the decomposition of the $(M + H)^+$ ions are the most intense[43] (Fig. 1).

According to some data,[40-42] the average yield of the protonated ions from a film of an organic compound is 0.1; however, even for related compounds the values of $S^{\pm}$ differ markedly. In respect of aminoacids the yields of the ions $(M + H)^+$ from glycine and leucine differ by a factor of 150, while the ratio of the peak intensities of the fragment ions $(M - COOH)^+$ and $(M + H)^+$ varies from 10 in the alanine spectrum to 0.1 in the leucine spectrum.[42] A detailed study of the dependence of the yields of the ions $(M + H)^+$ and $(M - H)^-$ in the glycine spectrum on the experimental conditions showed that the ratio $(M + H)^+/(M - H)^-$ can be altered by a factor of 100 by changing the pH of the initial aqueous solution.[42] The yield of the ions $(M + H)^+$ increases with increasing acidity of the solution, while the addition of alkali promotes an increase of the yield of $(M - H)^-$. This is the first mention of the fact that the yield of ions under SIIE conditions can be altered and that for ionic compounds it is always higher than for neutral molecules. Using the zwitter-ionic character of the aminoacids, glycine has been converted[42] into one of the following ionic forms by the addition of acid or alkali:



Variants of this procedure for the conversion of the compound to be analysed into an ionic form was subsequently widely employed in studies by other investigators.

The possibility of changing $S^{\pm}$ makes it necessary to indicate the conditions used to prepare secondary ions in the determination of the sensitivity of the SIIE method. Benninghoven[51,52] estimated the limits within which substances of different types can be detected, assuming that not less than 10% of the number of molecules of the test substance on the target leave the surface in the form of quasi-molecular ions. If 10^{-10} of a mole of the product, i.e. 6×10^{13} molecules, have been deposited on the support, then in such a case 6×10^5–3×10^{12} ions arrive on the detector, depending on the type of mass-spectrometric analyser used (the relative aperture varies from 10^{-7} for static magnetic instruments with double focussing to 0.5 for time-of-flight instruments). Under ion counting conditions, it is possible to record reliably the signal from 1000 ions; consequently the limit for the detection of organic substances with the aid of SIIE is in the range 10^{-12}–10^{-19} of a mole. However, under real conditions, such high sensitivity cannot be achived owing to the presence of "chemical noise" and peaks due to admixtures.

Benninghoven[53] demonstrated the high sensitivity of the SIIE method in the solution of a practical clinical problem, namely the identification of medicinal drugs in urine. Narcotic drugs (morphine, codeine, meperidine, methadone) were introduced artificially into urine in an amount equivalent to 1 mg per 100 ml. A dilute (1 : 20) solution of 1 μl of urine (~0.5 g of each drug) was deposited on a support, which was placed in the focus of the primary ion beam. The $(M + H)^+$ ions from each preparation (Fig. 2) and certain fragments were observed in the mass spectra. Sodium cyclohexene-sulphonate introduced into the organism in an amount of 200 mg was not detected in the patient's urine after 12 h, but, when 18 h elapsed, its presence was demonstrated in an amount of 6.2 mg ml^{-1}.[53] The possibility of identifying 10^{-10} g of phenylalanine on a commercial double foccussing instrument

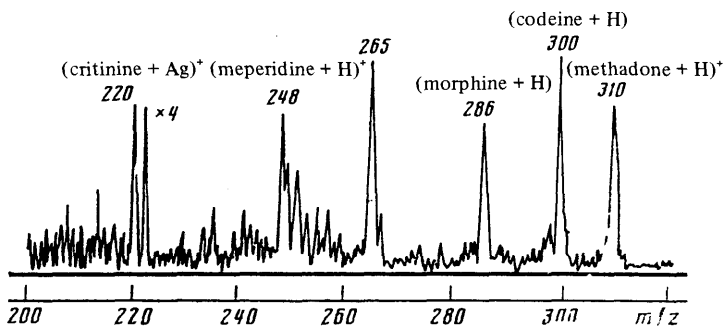


Figure 2. A fragment of the secondary emission spectrum of a mixture of narcotic substances.[53]

(Varian 311 A) has been reported.[54] The combination of the SIIE method with a time-of-flight analyser is especially promising. This application has been developed in a number of studies.[55–57]

Cooks and co-workers[58,59] were the first to initiate the development of another application of the SIIE method based on the ability of the majority of organic molecules, particularly highly polar ones, to form complexes with alkali metal cations on bombardment with the primary beam. The authors published their communication one year after the publication of the first study by Benninghoven and co-workers,[42] where the intensities of the $(M + Ct)^+$ ion peaks in the mass spectra were smaller by an order of magnitude than those of the $(M + H)^+$ peaks and their appearance was attributed to incomplete coverage of the surface of the metal support by the layer of the specimen. This hypothesis was subsequently confirmed experimentally; the composition of a flux of secondary ions from a surface coated by an aminoacid (glycine, α- and β-alanine, and serine) has been investigated with the simultaneous observation of the surface layers with aid of X-ray[60,61] and Auger spectrometers.[61] On the grounds that the cationated complexes $(M + Ct)^+$ are more stable than the protonated ions $(M + H)^+$ [56,57,62,63] [the protonated adenosine 5-monophosphate protonated ions have a lifetime ≤10 μs, while that of $(M + Na)^+$ is greater at least by an order of magnitude[63]], Cooks and co-workers developed several procedures whereby it is possible to increase the content of the cationated ions in the spectra of test substances; the specimen was deposited on the support in a mixture with metal, sulphur, carbon, silicon,[64] and alkali metal salt powders[58,64–67] and was bombarded by ions of other elements (cobalt, copper and silver).[59,61,64] Complexes with 22 elements in the Periodic System have been obtained in this way.[37]

These methods of generation of TUC ions by the SIIE procedure rapidly found applications in studies by other investigators. A detailed investigation has been made[47,68] of the dependence of the yield of the ions $(M + H)^+$, (M + cation of added salt)$^+$, and (M + cation of the metal of the support)$^+$ for different aminoacids M deposited on the support in a mixture with LiCl. By adding sodium or lithium chloride, Japanese workers obtained secondary emission mass spectra of mono-, di-, tri-, and tetra-saccharides,[69–72] adenosine, and 13 aminoglycoside antibiotics.[70,72] The authors noted that the added salts increased the intensity of the peaks of the quasi-molecular ions and decreased the extent of their fragmentation. However, the excess salt reduces the $(M + Ct)^+$ peak intensity and in addition promotes an increase of the fraction of the $(M + 2Ct + H)^+$ ions, which complicates the interpretation of the mass spectra. Analogous results have been obtained in other investigations.[47,68] Cooks and co-workers, who detected the $(M + 2Ct + H)^+$ ions in the spectrum of aminobenzoic acid,[58] proposed a simple method whereby one can avoid such complications—the use of ammonium chloride as an additive.[66,73,74] In this case the $(M + H)^+$ ions appeared in the spectrum together with the intense peak of NH_4^+ ions.

The stabilities of the $(M + Ct)^+$ complexes differ for different cations. The alkali metal cations show a greater stabilising effect. In selecting the conditions for the solution of a specific problem, one must be guided by the following rules established by Grade and Cooks:[59] (a) the $(M + Ct)^+$ cluster is more stable the more polar the molecule [for example, the peak intensity ratio $(M + Ag)^+/M^+$ in the stilbene spectrum is 500 times greater, while that in the *p*-aminobenzoic spectrum is 1000 times greater than in the anthracene spectrum]; (b) the degree of fragmentation can be regulated by producing complexes with cations of different kinds; this can be done in the spectrum obtained under electron impact conditions by altering the energy of the ionising electrons. For example, in the ionisation of *p*-aminobenzoic acid on a support made of the Ag + Pd (60 : 40) alloy the peak intensities of the ions $(M + Ag)^+$ and $[(M - COOH) + Ag]^+$ were identical, while the ratio $[Pd + (M - COOH)]^+/(Pd + M)^+$ was 7. For molecules with a high electron affinity, an attempt was made to obtain anionated complexes; however, complexes with the Cl^- and CN^- ions were not detected among the negative ions in the mass spectra of o-, *m*-, and p-aminohydroxybenzoic and mercaptobenzoic acids, 1,5-dihydronaphthalene, pentachlorophenol, nicotinamide, and 1-hydroxyanthraquinone. The spectra contained intense peaks of the ions $(M - H)^-$, $M^{\cdot-}$, and $(M - H - CO_2)^-$. The ratio $(M - H)^-/M^{\cdot-}$ increases with increasing acidity of the product. It has been noted that the spectra of negative ions contain few lines and can be readily interpreted. The interpretation is especially facilitated by comparing the spectra of positive and negative ions derived from the same product.[75]

Thus, using the ability of organic molecules to give rise to complexes with cations, it is apparently possible to obtain the mass spectra of compounds with a high molecular weight and a high polarity. These studies have only just begun. Hitherto it has been possible to obtain the quasi-molecular ions of methylated nucleosides[67] and polynucleotides[76] and it has become possible to carry out the mass-spectrometric analysis of the compositions of certain DNA and RNA after their completely enzymic hydrolysis. The mass spectra of saccharides,[69–73,77] including pentasaccharides[71,77] and octasaccharides,[72] adenosine, certain antibiotics[72,78] and oligopeptides[79,80] have been published. The aminoacid sequence in peptides can be determined from such spectra using the method of activated collisions.[80]

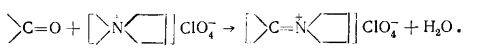
In estimating the sensitivity of the method employing cationated molecular ions, it is essential to take into account the differences between the capacities of the test substances for complex formation. The limit of the detection of sucrose in the mixture with LiCl proved to be 10 ng when the $(M + Ct)^+$ signal is 5 times more intense that the noise, while for adenosine the $(M + Ag)^+$ limit is 2 ng.[81] The sensitivity for glucose in a mixture of NaCl proved to be higher than 10^{-11} Cl g^{-1}.[69]

The mass spectra of organic ammonium salts and their analogues have been studied in detail under SIIE conditions.[81–87] Instead of complexes of the molecules with a proton or cation, the secondary ions are found to comprise undecomposed organic cations, some of which break down, giving rise to fragments which make it possible to infer the composition of the salt cation. Diquaternary salts do not give rise to dications in the vast majority of cases;[86] sometimes charge separation takes place, i.e. two singly-charged fragments of the dications are produced or a singly-charged cation is formed by loss of a proton.[87]

Comparison of the efficiencies of ion formation for ionic organic salts and compounds forming complexes with Ct has shown that the yield of ions derived from the quaternary ammonium salt $(C_2H_5)_4N^+I^-$ is 100 times greater than that of the ions derived from the mixture of dicyanobenzene and a copper(II) salt under identical conditions.[82] The absolute limit of the detection of the salt from the peak of the cation was 10 ng cm^{-2} (the signal exceeded the noise over 1 min).[81] A high sensitivity has been demonstrated in the identification of choline and choline esters[84] and also in the determination of muscarine and choline in thin-layer chromatographic spots.[85]

Thus the sensitivity of the method is highest for ionic compounds. Several procedures have been proposed whereby organic substances can be made to undergo a transition to a

formally ionic state; these transformations have been called a new type of "derivatisation".[87-89] For example, amphoteric compounds can be converted into an ionic form by adding inorganic acids or alkalis. As shown above, the addition of salts to basic products also increases the yield of quasi-molecular ions since metal ions are Lewis acids. By mixing amines with suitable alkyl iodides, it is possible to obtain the salts of quaternary nitrogen bases. On interaction with pyrrolidinium perchlorate, aldehydes and ketones are converted into immonium salts:



The proposed procedures extend the range of substances giving rise to intense quasi-molecular ions and characteristic fragments under SIIE conditions. Compounds not susceptible to analysis under field desorption conditions can nowadays be identified by the SIIE method. For example, after unsuccessful attempts to detect the ions of cymostatine and other thermally unstable antibiotics, the mass spectra of these molecules were obtained[78] by bombarding the specimen (in a mixture with NH_4Cl) by Xe^+ ions.

The determination of quantitative data concerning the mixture of organic products from the recorded secondary-emission mass-spectra is not always possible. In some investigations[67,76,90] the concentration of one of the components was estimated from secondary emission mass-spectrometric data using an isotopic isomer of the compound analysed as the internal standard. However, in many instances[81,91] it has been observed that formation of the ions of certain components is suppressed in the bombardment of a mixture of substances by the primary beam. For example, the spectrum of a mixture of five narcotic substances placed on a support was found to contain the $(M + H)^+$ ions derived from only three compounds.[91]

Summarising the data obtained in studied of thermally unstable compounds by the SIIE method, the following conclusions can be reached:

1. The spectra contain the intense peaks of the $(M + H)^+$, $(M - H)^-$, and $(M + Ct)^+$ ions, which make it possible to determine the molecular weight of the test substance.

2. Ionisation takes place in the solid state at room temperature or after slight heating; thermal degradation was not observed under these conditions.

3. The degree of fragmentation of the organic molecule can be regulated by altering the type of metal cation in the complex $(M + Ct)^+$ ion.

4. The method is highly sensitive, particularly for organic salts and polar compounds. Its sensitivity with respect to the three types of ion peaks decreases in the sequence organic cation > cationated molecules > protonated molecules. Under real conditions the determination of the mass spectrum under conditions where the support with an area of 0.1 cm^2 is scanned, it is necessary to deposit 10^{-10}–10^{-7} g of the test substance when the analyser employed is a commercial mass spectrometer with double focussing.[53,70]

5. The method can be used to identify products separated by thin-layer chromatography; in order to record the mass spectrum, the spot bombarded must contain at least 10 μg of the product. The first positive results using the SIIE method in a liquid chromatography–mass spectrometer system have been obtained.[46,92,93]

6. The method of preparation of the specimen for analysis is very simple and does not require a high experimental skill and lengthy preparations, as happens for example, in analysis by the FD method.

2. Secondary Atom–Ion Emission

The replacement of the primary ion beam by a beam of accelerated neutral particles has led to new possibilities for the study of involatile highly polar and thermally unstable compounds by the mass-spectrometric method. Data demonstrating that irradiation of the specimen by accelerated atoms makes it possible to ionise without decomposition heavier molecules than under SIIE conditions were surveyed towards the end of 1981.[94] For example, it has been possible to record the quasi-molecular ions of glucagon (a pancreatic hormone; MW = 3841) and the B-chain of insulin, separated from the rest of the molecule by oxidising disulphide bridges (MW = 3494).[95] The mass spectra of other biologically important products, obtained on bombardment with a beam of accelerated atoms have been published in reviews.[23,96-98] Compounds with MW > 4000 could be analysed at that time only by the plasma desorption method, with the aid of which the quasi-molecular ions of an oligonucleotide with MW = 6278 were recorded. However, by selecting the optimum balance of sensitivity and resolution, the spectra of protonated molecular ions derived from the hormone adrenocorticotropin (MW = 4538) and the undecomposed ox insulin molecule (MW = 5730) were obtained as early as 1982 on a magnetic mass spectrometer with suitable characteristics using the atom–ion emission (AIE) method[22] [FAB in Western literature (Ed.of Translation)].

The AIE method was developed and used for the first time by Tantsyrev and Kleimenov in 1973 in order to obtain the mass spectra of involatile organic molecules.[99] The object of the study consisted of thin films of polymeric substances deposited on a metallic support. The surface of the specimen was bombarded with a beam of Ar atoms having an energy of 300–3000 eV and a flux density of 10^9–10^{10} atom s^{-1} cm^{-2}. The AIE method proved to be convenient for the analysis of polymers, each of which has its characteristic spectrum suitable for its unambiguous identification; the spectra of copolymers represent a superposition of those of each polymer.[99-101]

The mutual orientation of the monomeric units in the macromolecules could be established from mass-spectrometric data[102-105] by determining the relative contents of hydrogen and deuterium when polymerisation took place with participation of a deuterium-containing monomer.[106] Apart from macromolecules, Tantsyrev and co-workers investigated the secondary-emission mass spectra of several TUC (aminoacids, secondary ammonium salts, and bases),[107] while in 1981 a systematic investigation of the mass spectra of biological substances was begun.[108-111]

In the non-Soviet literature Barber and co-workers or Surman and Vickerman (Great Britain), who published simultaneously in 1981 the secondary-electron mass spectra of several organic compounds,[112,113] are regarded as the discoverers of the AIE method as a new procedure for the ionisation of TUC. The rate of development of this new method, whereby it is possible to ionise without decomposition unstable organic molecules, is extremely high. Thus Barber and co-workers alone published in one year following the appearance of their first communication[112] not less than 17 papers devoted to the study of the mass spectra of bio-organic compounds of different classes.[22,114-129] At the present time the AIE method is widely used by many teams of investigators.[98,130-139]

The rapid spread of the new method for the ionisation of TUC is determined not only by the large amount of information derivable from the AIE spectra but also by the fact that their measurement does not require a major modification of commercial mass spectrometers.[140,141] On the basis of ion

gun designs proved a long time ago, the Kratos Company began the manufacture of AIE sources for the AEI MS902 apparatus,[117] while the Varian Mat company developed a design for a source with ionisation by an atomic beam for the MAT 731 mass spectrometer.[142]

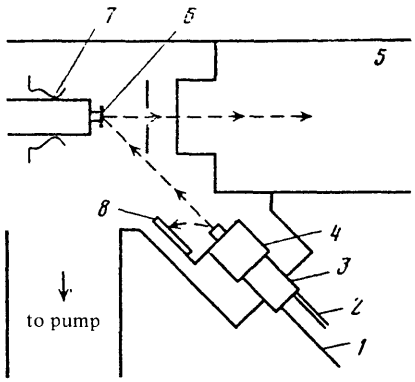


Figure 3. Schematic illustration of the ion source with the specimen bombarded by a beam of atoms[196] 1) high-voltage power supply; 2) injection of an inert gas; 3) region in which the primary ions are formed; 4) charge-transfer chamber; 5) mass analyser; 6) target with specimen; 7) vacuum lock; 8) deflecting electrode.

An apparatus has been described in which the secondary ions obtained as a result of ionic bombardment are separated by means of a static analyser with ordinary focussing;[143,144] a combination with quadrupole analysers is most frequently employed.[145] In order to obtain an accelerated atomic beam (usually a beam of Ar or Xe atoms), the ion beam initially generated is passed through a collision chamber. Fig.3 presents a systematic illustration of the AIE source. Ions undergo charge transfer on collision with the corresponding atoms in a collision chamber *4* filled with the gas from which the ions have been derived. The charge transfer cross-section is in this case large (10^{-16}–10^{-15} cm^2) [146] and approximately 50% of the ions undergo charge transfer without significant scattering of the beam in a chamber 100 mm long at a pressure of 10^{-4} mmHg.[104,146] An increase of pressure in the collision chamber by an order of magnitude decreases the degree of conversion of the ions into atoms to 10–30%.[143] The particles retaining the charge are removed from the beam by means of a special electrode *8*. The energy of the atom beam (of the order of magnitude of keV) differs somewhat from the nominal value of the applied potential difference accelerating the ions.[142] The beam of atoms bombarding the target *6* generates the maximum number of secondary ions at low angles of incidence relative to the target plane. Bombardment at an angle close to 90° leads to an increase of the fragmentation of the test molecules. The heavier the particles in the primary beam, the higher the yield of secondary, particularly quasi-molecular, ions.[94] For example, bombardment with mercury atoms increases the yield of the quasi-molecular sucrose, raffinose, and certain aminoacid ions by a factor of 10 relative to bombardment with Ar atoms.[147]

The principal distinctive feature of the preparation of secondary ions under AIE conditions involves the use of liquid targets made from volatile substances. A solution or a suspension of an organic compound in a liquid with a low vapour pressure is bombarded by accelerated atoms. This procedure has apparently led to the successful preparation of undecomposed quasi-molecular ions derived from extremely unstable and heavy biomolecules. Liquid targets were first used to obtain SE spectra by Tantsyrev, who showed that poly(propylene glycol) constitutes a convenient liquid target.[146] Glycerol is nowadays most often used as the involatile liquid, to which a small amount of an electrolyte, for example, oxalic acid, is added to ensure conductivity. The vapour pressure of glycerol at room temperature does not exceed 1×10^{-4} mmHg.[148] Apart from glycerol, epoxypropane,[139] organic and silicone oils,[95,128,149] α-monothioglycerol and its mixture with tetraethylene glycol,[95] polyglycol,[131] triglycerol, poly(ethylene glycol),[150] diethanolamine, tetraglyme, etc.[151] have been tested as solvents.

The application of liquid targets in AIE freed experimenters from many disadvantages characteristic of the SIIE method. Firstly, during bombardment by ions a positive charge is developed on the surface of the solid specimen, which must be compensated by a specially generated dark electron current. Otherwise, broad peaks, displaced towards higher mass numbers relative to integral mass peaks, appear among the recorded secondary ions peaks.[152] Charges do not accumulate on the surface of a liquid conducting target even in the presence of a small fraction of charged particles in the primary atom beam.[142] Secondly, bombardment with an atom beam makes it possible to employ lower potentials in the ion source in order to control the secondary ions; finally, under AIE conditions, the signal/noise ratio is higher by an order of magnitude than on irradiation with an ion beam.[80]

The role of the liquid phase in the mechanism of the transfer of the primary beam energy to organic molecules on the support has been investigated,[153–155] but is not as yet entirely clear. In a liquid the extent of the decomposition of the specimen molecules under the influence of high-energy primary particles apparently diminishes. On the other hand, the surface of the target is constantly renewed by undamaged portions of the specimen as a result of diffusion from internal layers. Furthermore, it has been shown[95] that certain test compounds shows an excess surface concentration, relative to the bulk-phase concentration, associated with the presence of hydrophobic groups. If these hypotheses are correct, liquid targets can be irradiated by a high-density primary beam without maintaining static bombardment conditions (for atom beams not exceeding 10^{10} atoms s^{-1} cm^{-2}), only making sure that the target does not become heated. An increase of the primary beam density entails an increase of the yield of secondary ions, i.e. ultimately leads to a diminution of the limiting concentrations of the products detected by the AIE method.

Serious experimental tests of the above postulates have not so far been published, but the advantage of liquid targets has been rapidly demonstrated and they have come to be used not only in AIE but also in the latest investigations by the SIIE method. This new procedure make it possible to obtain under SIIE conditions quasi-molecular ions derived from heavier and more unstable compounds.[77,80,156–158] It has been suggested that there are no radical differences between SIIE and AIE [89,115,139] and that the achievements by the AIE

method in the analysis of TUC are due mainly to the use of liquid targets. This has been confirmed by our study,[77] in which the use of a liquid target (diethanolamine) made it possible to obtain the quasi-molecular ions derived from an eight-membered cyclic oligosaccharide, namely γ-cyclodextrin (MW = 1679) on bombardment with Xe^+ ions. In the absence of a liquid matrix, it was possible to record only the ions of the tetrasaccharide stachyose (MW = 666).[71] Although quasi-molecular ions of heavier and more complex compounds have been obtained by the AIE method, the use of liquid targets in the SIIE method reduces the difference between the two procedures. In the future a liquid matrix will probably become an essential element of the study regardless of whether the specimen is ionised by a beam of atoms or ions. For the successful ionisation of different bio-organic substances, it is necessary in each case to select an appropriate liquid target matrix.[77,154] The elucidation of the role of the liquid phase in the ion formation mechanism has become an urgent taks in theoretical and experimental studies.

The mass spectra of organic compounds investigated under conditions involving irradiation with an atom beam do not show significant differences from the mass spectra recorded on bombardment with an ion beam.[94,147,157] A distinctive feature of the spectra obtained on a liquid target is the presence of the matrix ions. The molecules of the liquid appear in the spectrum in the form of cluster ions and fragments. For example, for glycerol (G) these are the positive ions $(G_n + H)^+$, $(G_n + Na)^+$, and to a lesser extent $(G_{n-1} + G - H + Na)Na^+$, where n reaches 15.[111] Clusters in which the molecules of the solvent and the test substance are combined sometimes appear. The spectra of negative ions contain significantly fewer clusters.[95] The presence of cluster ions has been used for the exact determination of the molecular weight of the test compound.[156] A method has been proposed for calibrating the mass scale under AIE conditions on the basis of the reference peaks of clusters comprising calcium toluenesulphonate and glycerol.[159]

Summarising the possibilities of the AIE method, we may note that the method increases the accuracy of the determination of the molecular weights of heavy molecules, since the $(M + H)^+$ and/or $(M + Ct)^+$ ions are always present in the spectra. The identification of the quasi-molecular ions among the peaks in the region of heavy masses is facilitated by comparing the mass spectra of positive and negative ions. The latter do not contain complex cluster ions and the heaviest peaks are due to the $(M - H)^-$ ions. The spectra of fragment ions make it possible to obtain information about the structure of the test compounds. The stability of the AIE spectra in time makes it possible to record the peaks of metastable ions, which are used to determine the mode of fragmentation of the test molecule.

The AIE method does not require the chemical modification of the test compounds, increases the reliability of the results, and diminishes by a factor of hundreds the amount of the test substance required for the analysis (for example, 1 μg instead of 1 mg is sufficient for the analysis of antibiotics[120]). These properties of the method altered radically the mass spectrometric procedure established previously for the determination of the aminoacid composition of peptides, in which chemical modification of the compounds was an essential stage.[3] The interpretation of the AIE mass spectrum yields nowadays information about the aminoacid sequence and about the composition of the terminal N- and C-acids.[114,115,118,119,121,130,132,161–163] The determination of the molecular weight of the peptide requires 0.1 nmol of the specimen and the determination of the aminoacid sequence requires 2–50 nmol.[24] However, one should note that sometimes not every aminoacid is represented in the spectrum by an individual peak.[132]

The high sensitivity of the AIE method is manifested in the analysis of bioproducts of different classes; data have been obtained for the molecular weights and structures of saccharides,[22,98,123,163–165] nucleotides and nucleosides,[24,117,137,166,168] lipids,[151,167,169] aminoglycoside and peptide antibiotics,[116,120,170,171] steroids,[23,134] sulphonated azo-dyes,[124–126] and a number of other compounds.[24,117,133,135,151,172] The identity of the AIE spectra of the synthesised and natural products has come to be regarded as confirmation of the structures of the natural products.[138]

Identical detection limits have been found in the mass spectra of positive and negative ions.[24] In order to increase the intensity of the quasi-molecular ions, the same procedures for the conversion of the test molecules to an ionic state are used in the AIE method as in the SIIE method.[88,95,117,124,132,173]

The quantitative aspects of the AIE method have not as yet been developed. However, the attempts to estimate the contents of the components in a mixture from the peak intensities of the quasi-molecular ions have already been made. Thus the determination of an admixture of a monomethyl-substituted quaternary amine in a mixture of dimethyl-substituted quaternary amines $(CH_2)_2N^+R^1R^2Cl^-$, entering into the composition of beef fat, has been reported.[23] The admixture concentration obtained (10%) agrees well with the result of chromatographic analysis (7.7%). At the same time it has not been possible by the AIE method to determine quantitatively nitrogen-containing cyclic compounds present in fuel shale,[131] although the qualitative identification of the individual components has been achieved successfully. The attempt to determine the content of bleomycins A_2 and B_2, differing only in the composition of the *N*-terminal aminoacids, also failed. The intensities of the formation of ions from these related compounds under AIE conditions differed appreciably.[116] A study has been made[174] of the causes of this phenomenon in order to obtain quantitative data for the dissociation constants of weak acids in solution.

The simplicity of the procedure used to prepare the specimens to carry out the analysis have led to an increasing use of the AIE technique for the measurement of the spectra. It is displacing the FD method, which has been for a long time the principal procedure for the analysis of TUC. Extensive factual data concerning the determination of the compositions and structures of biomolecules by the AIE spectroscopic method can be found in reviews.[89,98,145,151,175]

The principal difficulty, involving the preparation of ions from thermally unstable highly polar heavy molecules, has been overcome by the AIE method. Whereas several years ago the low volatility and stability of the test products constituted the main obstacle in mass-spectrometric analysis, at present the limiting factor has been the maximum capacity of mass analysers as regards the range of masses and their resolving capacity in the recording of heavy quasi-molecular ions generated under AIE conditions.[22]

3. Bombardment with High Energy Ions

A new method called desorption by high energy ions (DHEI),[176] which makes it possible to record the mass spectra of TUC by irradiating the latter with like multicharged ions speeded up in accelerators to energies ranging from several units to several tens of MeV, has been proposed recently. The general form of the mass spectra obtained is characteristic of secondary ion emission and differs little from the SIIE and AIE spectra. A distinctive feature of the

new method is the possibility of altering within wide limits the yield of the secondary ions as a function of the mass, charge, and energy of the primary beam ions (in contrast to the bombardment of the specimen by the ^{252}Cf fission fragments, whose composition is inhomogeneous and whose charge and energy vary independently of the experimental conditions).

The mass spectra of valine, obtained by bombarding a solid film of the specimen deposited on a nickel support by ^{16}O, ^{18}O, and ^{32}S ions in different charge states with energies ranging from 0.1 to 50 MeV, have been investigated.[176-180] The primary beam density was 10^3–10^4 ions s^{-1} cm^{-2} and the angle of incidence was 30° (relative to the plane of the target). The peaks of the ions $(M + H)^+$, $(M + 2Na - H)^+$, and the highly intense peak of the $(M - COOH)^+$ fragment were detected in the mass spectra. The curve for the efficiency of the generation of the $(M + H)^+$ and $(M - COOH)^+$ ions contains two maxima, corresponding to the energies of the bombarding ^{16}O and ^{32}S ions of 10 keV and 8 MeV, regardless of the energy of the particles from the primary beam.[178]

In order to explain the observed phenomenon, two mechanisms of the interaction of the primary beam with the substance of the target have been proposed. On impact by relatively slow primary particles (up to 0.1 MeV), their energy is scattered in elastic collisions of the atomic nuclei, while the energy of fast particles (tens of MeV) is consumed mainly in the electronic excitation of the molecules.[94] The irradiation of the surface valine film by ^{18}O ions with energies of 20 and 25 MeV in different charge states has shown that, with increase of the positive charge of the bombarding ions, the yield of the secondary ions also rises.[179] It has been shown[91] that the relative yield of the ions $(M + H)^+$ derived from Gly – Gly increased by a factor of 20 following the replacement of the primary beam of Cs^+ ions with an energy of 3 keV by Ge^{4+} ions with an energy of 54 MeV. The effect of raising the charge state is greater when compounds with a molecular weight in excess of 1000 are bombarded. The yield of secondary ions increases sharply with decrease of the angle of incidence of the primary beam relative to the plane of the target.[181]

The mass spectrum of a peptide with a molecular weight of 6000 has been obtained by the DHEI method;[91] following the bombardment of a thin film of ox insulin by ^{127}I ions with a 20-fold charge and an energy of 90 MeV, the mass spectra of positive and negative ions, containing peaks in the range of the molecular weights of the A- and B-chains of insulin, were recorded.[182]

The advances made have shown that, despite the complexity of the apparatus, the DHEI method can be used successfully to obtain the mass spectra of TUC, although so far only the first steps have been taken in this direction.

III. PLASMA DESORPTION BY ^{252}Cf FISSION FRAGMENTS

A new method for the analysis of involatile and relatively involatile TUC, called the method of plasma desorption by ^{252}Cf fission fragments (PlD ^{252}Cf), was developed in 1974.[183-187] The ions of the test substance are formed in the following manner: the test specimen is deposited on a thin foil behind which a ^{252}Cf source is placed. Quasi-molecular and other ions arise as a result of the penetration into the specimen of the ^{252}Cf fission products. The energy liberated under these conditions (~1000 eV $Å^{-1}$) causes the formation of a heat pulse in the specimen up to 20 000 K lasting 10^{-12} s. A cylindrical microvolume of the specimen-support with a radius of 25 Å is converted into a hot gas in which molecules of the specimen and of the support react. The ionic products of these reactions are "withdrawn" by an external electric field and are analysed in the mass spectrometer.

The spontaneous fission of the ^{252}Cf nucleus results in the formation of two fragments with unequal masses. There is a possibility of the formation of up to 40 pairs of different particles, but the formation of $^{142}Ba^{18+}$ and $^{106}Tc^{22+}$ with kinetic energies of 79 and 104 MeV respectively is most probable. The pair of fission fragments arises simultaneously (within 10^{-9} s), which leads to exceptional possibilities for the employment of the time-of-flight technieque for the recording of the mass spectra.[184,185]

The main difficulties in the employment of this method consist in the high radioactivity of the source, which usually amounts to 10–100 microcuries and in the high toxicity of ^{252}Cf. The preparation of the source is therefore a complex task.[184,187] The source is obtained by evaporating a drop of a ^{252}Cf solution deposited on a nickel or aluminium foil 1–5 μm thick; it is then covered by a polychloroacetate film, which prevents the migration of ^{252}Cf on the surface of the foil. In order to attenuate the intensity of the source, the latter can also be covered by additional layers, for example, gold.[186,187]

The specimen in the form of a thin homogeneous film ~100 mg cm^{-2} thick is usually obtained by electrosputtering.[188-190] When the film is obtained by other procedures—by depositing a drop from the solution, by cataphoresis, etc., poorly reproducible results are obtained.[188-191] The limit of sensitivity depend on the type of molecules investigated; for aminoacids, it is of the order of 10^{-9} g cm^{-2}. The recording of the spectrum for the very lowest yield of ions takes ~12 h.[185,189,191]

In virtually all cases different modifications of the time-of-flight mass spectrometer are used to obtain the mass spectrum.[191-194] Its advantages are a theoretically unlimited mass range and the convenience of combining the method for the recording of ions with a pulsed ionisation method. The modifications of the mass analyser were made largely to increase the sensivity and the resolving power. In the range of heavy masses the accuracy of the mass number determined does not as a rule exceed hundredths per cent.[193-195] The inadequate resolving power of the time-of-flight mass spectrometers is a significant obstacle in certain investigations, for example, in the determination of the aminoacid sequence in peptides.[196-198]

The mechanism of the formation of ions in the PlD ^{252}Cf method has not been fully investigated, but the majority of investigators describe it qualitatively in the following manner. At the sites of incidence of the ^{252}Cf fission fragments local plasma zones arise in a specimen where the desorbed molecules are ionised by one of two pathways: (1) via the formation of ion pairs: $2MH \rightarrow MH_2^+ + (M - H)^-$. This pathway, which is most typical for aminoacids, peptides, nucleotides, etc., involves the transfer of a proton from the acid end of one molecule to the basic end of another. (2) Via ion–molecule reactions with H^+, Na^+, K^+, or H^- ions. This results in the appearance in the spectrum of quasi-molecular ions containing an atom of the corresponding alkali metal, while the spectrum of negative ions contains protonated quasi-molecular ions.[199,200]

Aminoacids,[183,201] peptides,[184,195,201] nucleotides,[194,196-198,202,203] saccharides,[164,188,201] chlorophyll a,[204,205] antibiotics,[192,206] polytoxins,[207,208] vitamins,[188,191,193] and steroids[188,209] have been investigated by the PlD ^{252}Cf method. The results of such studies are satisfactorily reproducible from experiment to experiment and from one group of investigators to another.[204,205]

At the present time the PlD ^{252}Cf method makes it possible to obtain the heaviest ions. The ions $(2M + Na)^+$ with a mass of 12 637,[210] derived from fully protected oligonucleotides (dodecanucleotide with MW = 6278), have been recorded in the analysis of oligonucleotides.

The spectra of the test substances contain in all cases the peaks of fragment ions together with quasi-molecular peaks. The number of fragments arising in the PlD ^{252}Cf method is large even for relatively small molecules. Many fragmentation processes can be satisfactorily explained in terms of the concepts adopted in the chemistry of gas-phase ions. This enabled Field and co-workers[201] to assume, in contrast to Danigel and MacFarlane,[194] that the PlD ^{252}Cf method cannot be classified as a mild ionisation method. The method should rather be treated as one possessing dual properties: it makes it possible to obtain the intense peaks of quasi-molecular ions like the classical mild methods, and at the same time it yields an extensive fragment spectrum as in severe methods, for example, under electron impact. Such duality is not observed for other high-energy ionisation processes.

Investigators have noted that the plasma desorption method is promising and has considerable possibilities for the study of various classes of high-molecular-weight organic substances. The advantages of the method include, firstly, the possibility of the simultaneous study of the spectra of positive and negative ions, which permits a reliable determination of the molecular weight, structure, and the concomitant impurities in substances such as fully protected ribo-oligonucleotides up to heptamers inclusive.[174–176] Secondly, it became possible to establish the sequence of groups in complex organic compounds without a preliminary chemical modification in the intermediate phases of the synthesis (see, for example, Yoshihara[187]). Thirdly, with the aid of this method one can investigate unstable dissociation products of the ionised molecules and their fragmentation in the drift tube of the time-of-flight mass spectrometer.[173,184] Their presence broadens the packet of ions and impairs the resolving capacity of the spectrometer in the same way as the change in the real diameter of the ionisation spot on the target, which is related to the parameters of the ion source.[172] Finally, the method is distinguished by the simplicity of the introduction of the specimen and the lack of necessity for a special preparation of the sample, which makes it possible, in particular, to set up on the basis of this method an LC–MS (liquid chromatograph–mass spectrometer) system. In the description of the LC–MS apparatus it is stated that the fractions separated in the liquid chromatograph were deposited by electrosputtering through a capillary onto supports placed on sectors of a disc rotating at discrete time intervals (12 positions at a pressure of 10^{-3} mmHg); the sectors with the sample were inserted in succession through a vacuum lock into the chamber of the time-of-flight mass spectrometer and were exposed to the ^{252}Cf source. The LC–MS combination has been used for the quantitative analysis of biochemical compounds, in particular, of antitumour preparations: etoposide, teniposide, and alkaloids vindesine, vinblastine, and vincristine.[189]

IV. LASER DESORPTION

The first information about the generation of positive ions by means of laser radiation dates back to the beginning of the 1960's[212] and at the beginning of the 1970's laser desorption was used for the analysis of organic substances,[213,214] including thermally unstable compounds with formation of a molecular ion.[215] However, up to 1978,[216,217] laser desorption and ionisation had not yet been regarded as methods for the investigation of organic substances; mainly the use of laser in the mass spectrometry of solids was reported in literature up to 1978 and the effects of the interaction of laser pulses of different power with the test substance were investigated and classified.[218,219]

After the laser irradiation of involatile substances (salts, nucleotide–Na_2, sucrose, peptides), the cationated molecular ions and certain fragments, yielding valuable structural information, are abundant in the mass spectrum.[220] Hence it follows that at certain intensities laser radiation is capable of causing the desorption of the ionised molecules and that laser desorption (a) constitutes a mild ionisation method and (b) is promising for the analysis of thermally unstable and involatile compounds by mass-spectrometric methods. Experiments designed to investigate the mechanism of the formation of the $(M + Ct)^+$ ions have also been carried out and studies have been made of the rapid heating processes and of the role of multiphoton processes which yield a fragment spectrum.[220–222] So far the laser desorption method has been used to investigate a large series of TUC and relatively involatile compounds: oligosaccharides,[216,223–228] nucleotides and nucleosides,[224,227,229,230] glucosides,[224,225,230] aminoacids and oligopeptides,[224,226–228,230,231] vitamins and antibiotics,[232] and other bioorganic compounds.[232,233] Mass-spectrometric data obtained with laser desorption have been surveyed in two reviews.[234,235]

Parameters of the lasers used in the study of organic specimens by the laser desorption method.

Test substance	λ, nm	τ, s	W, W cm^{-2}	E, J cm^{-2}	Refs.
Ruby	694	10^{-3}	$5\cdot10^{4}$	50	[237]
Neodymium	1 064	10^{-4}	$2.5\cdot10^{5}$	25	[237]
Neodymium	1 064	10^{-8}	$2.5\cdot10^{9}$	25	[237]
Neodymium	265	$1.5\cdot10^{-8}$	10^{7}	0.15	[241]
Ruby	347	$3\cdot10^{-8}$	10^{8}	3	[238]
Ruby	347	$3\cdot10^{-8}$	10^{8}	3	[230]
Neodymium	265	$8\cdot10^{-9}$	10^{8}	0.8	[230]
Neodymium	1 064	10^{-8}	10^{8}	1	[242]
Neodymium	1 064	$8\cdot10^{-5}$	$2.5\cdot10^{3}$	0.2	[226]
CO_2	10 600	$4\cdot10^{-8}$	$3\cdot10^{6}$	0.12	[243]
Ruby	694	$3\cdot10^{-4}$	10^{6}	300	[213]
Ruby	694	$3\cdot10^{-4}$	10^{6}	300	[214]
CO_2*	10 600	5	20	100	[244]
Neodymium	1 064	10^{-4}	$5\cdot10^{6}$	500	[224]
CO_2*	10 600	10^{-1}	10^{3}	100	[244]
CO_2	10 600	$1.5\cdot10^{-7}$	$8.7\cdot10^{6}$	1.3	[222]

Notation: λ is the wavelength, τ the duration of the pulse, W the power density, and E the energy density.

*Under continuous irradiation conditions; in the remaining cases pulse lasers were used.

Several methods, similar as regards experimental technique, have been proposed for laser desorption. The specimen is normally deposited on a copper grid from solution in ethanol or water and is irradiated by a pulse of focussed laser radiation. The laser desorption products are analysed in time-of-flight,[213–215,217,228,229,238] quadrupole,[227,236] static,[220–222,224,226] or other types of mass spectrometer.[231] A wide variety of lasers, both pulse-type and continuous emission, are used for irradiation in the range from infrared to the ultraviolet region of the spectrum (see Table).[234]

Laser desorption usually involves the formation of cluster ions of the type $(M + Ct)^+$, and H, Li, Na, K, Cs, Cu, Ag, and Pt can function as the Ct^+. In certain cases the negative $(M - H)^-$ ions are formed.[224,231,234] The mechanism of the formation of cluster and quasi-molecular ions in laser desorption is insufficiently clear and requires further theoretical and experimental studies. Cluster formation has been regarded[94,199] as the manifestation of various mild ionisation mechanisms. Numerous investigations of relatively involatile organic compounds by laser desorption methods indicate the possible occurrence of the following processes: vaporisation of molecules from the surface of the support under conditions of very rapid rise in surface temperature;[237,238] surface thermoionisation;[239] decomposition of molecules and ion–molecule reactions;[37] multiphoton ionisation processes.[223,224]

The Table presents the conditions in the formation of various groups of ions with the aid of lasers having different parameters.[224] Evidently the wavelength of the laser radiation does not have a significant influence on the character of ionisation. Quasi-molecular ions are formed when the power of the radiation is varied in the range from 10 to 10^8 W cm^{-2}, which casts doubt on the claim that multiphoton processes are essential for the formation of ions.[223,224] In the cases presented in the Table, the duration of the radiation pulses varied from 10^{-8} to 1 s, but in all cases ions were formed. Evidently, when low power pulse lasers are used, quasi-molecular ions are formed after a comparativley prolonged irradiation.[216,223] On the other hand, in the studies with powerful lasers the resolving capacity deteriorated with time and quasi-molecular ions could not be detected.[240] Analysis of the tabulated data also shows that the relation between the peak intensities of the quasi-molecular ions and the irradiation energies is determined by the material of the support.[222] If the material of the support is characterised by ready desorption (for example, in the case of quartz), then quasi-molecular ions are formed even for a low irradiation energy density; in the case of metallic supports, it is necessary to employ higher energy densities.

One may conclude that a definite minimum temperature, characteristic of the given specimen–support system and ensuring an energy balance of the system, is essential for the formation of quasi-molecular ions. The properties of the lasers (energy density, duration of pulses, the wavelength of the radiation) and those of the specimen–support system (energy absorption coefficient, thermal conductivity, heat of evaporation of the test substance, etc.) are taken into account in the balance. Lasers with a lower power density have been used in the study of the formation of quasi-molecular ions as a function of temperature.[94,200,220,245,246] The studies shows that it is possible to distinguish two temperature regimes: the lowest temperatures, at which neutral molecules are desorbed and higher temperatures at which surface ionisation and desorption of complexes with alkali metals are the most characteristic processes.[222] In all cases ion-molecule reactions in the gas phase, to which relatively involatile organic molecules are transferred without decomposition by the radiation, play a considerable role in all cases in the establishment of the final mass spectrum.

V. THE MECHANISMS OF ION FORMATION

It has been frequency noted that the mass spectra of organic and bio-organic molecules, obtained from the solid phase by different ionisation methods, are very similar. The similarity of the mass spectrum has been noted by many investigators.[51,54,66,67,94,139] Thus alanine and arginine, quaternary nitrogen-containing salts, sucrose, vitamin B_{12}, and adenosine 5-monophosphate give rise to identical mass-spectra under conditions where the specimens are bombarded by both potassium and caesium ions with energies ranging from 3.5 to 10 keV and ^{252}Cf fission fragments.[55] Under laser desorption conditions, ions can be formed with participation of thermal processes; nevertheless similar mass spectra of $(C_4H_9)_4N^+I^-$,[239] nucleotide bases,[239,240] and sucrose[239] have been obtained on irradiation of the solid products both by a low-power laser beam and by ^{252}Cf fission fragments. The spectra of sucrose recorded by the SIIE and LD methods are almost identical.[242]

The similarity of the mass spectra is determined by the following characteristics:

1. The principal ions in the spectra are even-electron particles. They include the quasi-molecular ions $(M + H)^+$ and/or $(M + Ct)^+$ and the cluster ions $(M + H)^+$, $(M + Ct)^+$, and $(M - H + 2Ct)^+$; in addition, odd-electron fragments (with odd mass numbers) appear in the spectra of compounds having the composition $C_xH_yO_z$. Tantsyrev and Saraev[248] compared the spectra of benzene obtained by the ionisation of the vapour and of a solid film (frozen on a support) by exposure to an atomic beam. The spectra had different intensities of the peaks, those due to odd mass ions proved to be significantly higher under conditions involving ionisation from the solid state.

2. The ions of organic substances leaving the surface are energetically stable. The internal energy of the secondary particles is low. The ionisation is accompanied by ion-molecule interactions. As a result, cluster ions and their fragmentation products appear in the spectra obtained by many of the methods discussed above.

3. Multistage decompositions are not characteristic of the spectra recorded. Only in the ionisation the atom-ion emission method (using a "light matrix") is it sometimes possible to record peaks of metastable ions.[249] Under the conditions of ionisation from the solid state, the recorded ions are formed during a very short time interval (several nanoseconds), which makes it convenient to combine these ionisation methods with time-of-flight analysers.

The similarity of the mass spectra discussed above permits the conclusion that the main processes involving the formation of the ions detected in the methods considered differ little from one another. Nevertheless, it was initially assumed that each ionisation method is based on an energy transfer principle characteristic only of that particular method. For example, it has been suggested that a beam of heavy multicharged ions with an energy amounting to tens of MeV transmits its momentum to the material of the support mainly as a result of electron retardation,[247] while the primary beam with an energy amounting to several keV is retarded as a result of interaction with nuclei.

We shall consider the question why the energy of the primary beam and the mass and charge state of the primary particles do not influence significantly the composition and ratios of the secondary ions in the spectrum of the given products. A common feature of all the methods involving secondary ion emission from the solid state is ultrafast transfer of momentum. When the specimen is bombarded by fast ions or atoms, the time interval during which energy is transferred amounts to 10^{-12} s, while on irradiation with a laser beam it is 10^{-8} s.[37,51] The short interaction time of the primary beam of particles or quanta with a layer of test molecules is the physical basis which justifies the combination in one group of all the ionisation methods considered. As a consequence of the ultrafast transfer of momentum, the organic molecules present on the surface at the site of impact receive, according to the majority of investigators, a small

amount of excitation energy. A rough estimate of its value under the conditions of ionisation by the $^{252}Cf^{+}$ fission fragments yield on average 1 eV.[199] This value has been confirmed by measurements in another study.[250] It becomes clear why quasi-molecular ions can be obtained in an undamaged form on exposure to a beam of ions with an energy exceeding by a factor of thousands or hundreds of thousands the bond energy in organic molecules. Theoretical calculations relating to the dynamics of the dislodgement of the ions of organic multiatomic molecules have shown that the probability of the expulsion of an undamaged molecular ion is fairly high.[251–255]

In order to account for the processes involving the formation of secondary ions on bombardment of a solid film of the test compound by a beam of fast atoms, Tantsyrev and co-workers were the first to put forward the idea of a "hot spot",[105,107,146,256,257] which reduces to the following statement: most of the energy of the primary beam is dissipated in a localised region—the "hot spot". As a result of a cascade of collisions, the set of molecules in the activated volume can be regarded as a highly heated dense gas. The size and depth of the "hot spot" depend on the character of the primary irradiation, but on the whole this mechanism explains the ion formation process in any of the methods examined, for example, that of Barber et al.[123] and Van der Peyl et al.[221] The transfer of momentum from the bombarding particles to the atoms or molecules of the target takes place isotropically, but in macromolecules with an ordered structure (polymers) the process has its characteristic features,[105,146] which will not be discussed here.

In the activated volume a fraction of the molecules are in a vibronically excited state and some are ionised. The positive and negative ions formed can leave the surface without undergoing any change. According to Benninghoven,[51] this is precisely the origin of the ions recorded in the SIE spectra. Cooks and co-workers[37,74,75,83] suggest that this mechanism is valid only for compounds with an ionic structure (for example, organic salts). When such compounds are irradiated, the "completed" ions are scattered" into a vacuum and no vibrational excitation of the ions takes place, since the process involving their formation resembles adiabatic expansion into a vacuum accompanied by cooling. Another portion of the ions formed within the hot spot are able to interact during their lifetime with the surrounding molecules on the surface. According to Tantsyrev, the cluster ions $(M_n + H)^+$ and $(M_n + Ct)^+$ arise in this way. This is not the only view in existence. Cooks and co-workers[39,73] suggest that the cluster ions appear as a result of ion–molecule interactions not on the surface but in the dense gas cloud above the spot. In one way or another, ion–molecule reactions make a significant contribution to the formation of secondary ions.

Finally a fraction of the secondary ions which have appeared are capable of undergoing unimolecular decompositions in the gas phase. The fragment ions produced make it possible to derive structure information from the SIE spectra. The three types of ions enumerated apparently determine the ionic composition of the mass spectra.

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The development of new methods for the ionisation of thermally unstable compounds over a short period has extended the scope of mass-spectrometric studies of the composition and structure of bio-organic compounds. This required in the first place a further improvement of the analytical components of the apparatus and of the methods for the determination and treatment of mass-spectrometric data and also the solution of many theoretical problems. It became necessary to increase the range of the mass numbers with the simultaneous retention of a high resolving power and accuracy of the mass determinations. The establishment of the overall formula of the test compounds (for MW in excess of 3000), taking into account the distribution of the intensities of the isotopic peaks of the quasimolecular ions, was found to be difficult.[258] The determination of the ion formation mechanisms and also the elucidation of the role of the liquid matrix in the formation of undecomposed ions of TUC with high molcular weights is important for the correct interpretation of the results of investigations.

Studies of the characteristic features of the unimolecular decomposition reactions of heavy organic ions in activated collisions under the conditions of tandem mass spectrometry have been initiated.[259] The possibility of combining the new ionisation methods with ion-cyclotron resonance spectroscopy is being considered.[260] Further development of these trends will undoubtedly extend the applications of mass spectrometry in studies on bio-organic compounds.

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Kinetics of the Oxidation of Mixtures of Organic Substances in the Liquid Phase

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The available literature data on the kinetics of the co-oxidation of organic substances by oxygen in the liquid phase are surveyed. The methods for the determination of the rate constants for reactions involving chain propagation by peroxy-radicals in the oxidation of mixtures are analysed and the experimental kinetic parameters of the co-oxidation of binary mixtures of organic compounds of different classes are presented. The general rules governing the kinetics of oxidation reactions in mixtures are considered and the methods whereby the rates and selectivities of the oxidation reactions of individual mixture components can be regulated are demonstrated.
The bibliography includes 111 references.

CONTENTS

I. Introduction
II. Kinetics of unbranched radical-chain oxidation reactions of mixtures
III. Methods for the determination of the rate constants for elementary reactions in co-oxidation processes
IV. Oxidation of binary mixtures of organic substances
V. The selectivity of the reactions of the components in co-oxidation

I. INTRODUCTION

One of the most highly developed fields in the study of oxidation reactions of organic substances is that of the theory of the homolytic oxidation of organic substances in the liquid phase. Detailed studies have now been made of the kinetics and mechanism of the oxidation of representatives of many classes of organic compounds,[1-5] but it should be noted that, because these processes yield reactive oxygen-containing products, which subsequently react, the oxidation of the individual substances takes place only in the very initial stage of the reaction. In subsequent stages the process proceeds as the coupled oxidation of the starting material and its primary oxidation products, which is normally the main cause of the low selectivity with respect to the required product at advanced stages of the reaction.

In order to regulate the oxidation process and to increase its rate and selectivity, it is necessary to known the fundamental features of the joint oxidation of various substances and in particular the parameters of the so-called "cross" reactions needed to establish the relations between the structures and the reactivities of molecules and radicals in elementary oxidation reactions.

Investigations of the oxidation of mixtures has now yielded many results important for the theory and practice of liquid-phase oxidation. These include primarily the discovery of systems where the intermediate radicals derived from one substance function as the reactants in the reaction with another substance in the course of the oxidation process, which leads to the formation of the desired product. An example of such a reaction is the joint oxidation of aldehydes and unsaturated hydrocarbons which has been studied in detail by Emanuel' and co-workers.[6-9] This reaction has been proposed[6] as an effective method for the preparation of olefin oxides.

Numerous studies have been devoted to the coupled oxidation of olefins and aldehydes (see Filippova and Blyumberg's review[10]). It has been shown that[11-13] critical phenomena are observed in the oxidation of mixtures of decane with ethylbenzene, which is due to the reactions of alkyl radicals with the hydrocarbons; the contribution of these reactions to the overall process kinetics is very considerable and controls the characteristic features of the process under the given conditions. The coupled oxidation of benzene and alcohols by molecular oxygen in aqueous solutions at 430–470 K has been investigated.[14,15] Benzene is resistant to oxidation under these conditions, while under co-oxidation conditions phenol is formed and the hydroxylating reagent is in this instance the peroxy-radical $HOO^{\cdot}$. Coupled reactions leading to the decarboxylation of organic acids both in their individual oxidation and in mixtures with other substances have been studied in detail;[4,16] the kinetic features of the process have been established. The influence of various factors on the kinetics of the coupled oxidation of benzene and cyclohexane at 460–520 K has been studied.[17,18]

The kinetics of the joint oxidation in systems containing aromatic alkyl-substituted hydrocarbons and benzaldehyde have been investigated.[19,20] Studies have been made[21-24] of the kinetics of the joint oxidation of lower olefins and the considerable influence of the mixture composition and reaction conditions on the yield of the olefin oxide and the oxidation products has been demonstrated. Aspects of the practical applications of the oxidation reactions of mixtures of hydrocarbon have been examined.[25,26]

The studies on the joint oxidation of organic substances in the liquid phase can be divided by convention into two groups. The first includes studies of the reactions occurring under the conditions of a branched chain process, which continues until advanced stages, and the process kinetics are described in this instance by a cumbersome system of non-linear differential equations whose solution is possible only by numerical methods with a computer. Theoretical analysis of the kinetics of such processes involves many difficulties and can be achieved only in isolated simplified cases. The other group of studies has been devoted to the co-oxidation processes occurring under the conditions of an unbranched chain

reaction to low degrees of conversion of the starting materials. Here the reaction scheme is much simpler and there is a possibility of determining the kinetic parameters of all the elementary steps. The results of studies of the second group are mainly discussed in the present review.

II. KINETICS OF UNBRANCHED RADICAL-CHAIN OXIDATION REACTIONS OF MIXTURES

Rigorous analysis of the kinetics of the oxidation reactions of mixtures is greatly facilitated when the reaction is carried out under conditions such that there is no chain branching. The kinetics of the oxidation of binary mixtures under the conditions of an unbranched chain reaction were investigated and analysed for the first time by Walling and McElhill,[27] who used the familiar Mayo-Walling copolymerisation equation[28] to describe the dependence of the rate of oxidation on composition. Subsequently this equation in one or other modification was used in the study of many binary mixtures of organic substances.

The general approach to the solution of the kinetic problems arising in the description of unbranched chain processes in multicomponent systems involving free radicals of different structure has been developed by Tsepalov.[29] Using this approach, it is possible to describe the kinetics of the co-oxidation reactions occurring with quadratic, linear, or mixed chain termination and also under the conditions of low oxygen pressures where one cannot neglect the reactions of alkyl radicals. The only limitation to its application is the need for fairly long chains.

In relation to the simplest case, namely the oxidation reaction of a multicomponent mixture occurring with long chains and initiated at a rate W_i at an oxygen pressure ensuring the complete conversion of alkyl radicals into peroxyradicals and with quadratic chain termination, the reaction mechanism can be formulated as follows:

$$\begin{gathered} R_iH \rightarrow R_i^{\cdot}, \\ R_i^{\cdot} + O_2 \rightarrow R_iO_2^{\cdot}, \\ R_iO_2^{\cdot} + R_jH \rightarrow R_iOOH + R_j^{\cdot}, \\ R_iO_2^{\cdot} + R_jO_2^{\cdot} \rightarrow \text{inactive products.} \end{gathered} \qquad (1)$$

The subscripts i and j vary from 1 to n, where n is the number of components. Under stationary conditions and for long reaction chains, the following equations are valid:

$$W_i = \sum_{ij} k_{tij} [R_iO_2^{\cdot}] [R_jO_2^{\cdot}], \qquad (2)$$

$$\sum_j k_{pij} [R_iO_2^{\cdot}] [R_jH] = \sum_j k_{pij} [R_jO_2^{\cdot}] [R_iH]. \qquad (3)$$

The system of equations can be formulated thus:

$$\sum_j (k_{pij} [R_jH] - b_i\delta_{ij}) [R_jO_2^{\cdot}] = 0, \qquad (4)$$

where

$$b_i = \sum_j k_{pij} [R_jH],$$

and δ_{ij} is the Kronecker delta. Solutions of this system have the following form:

$$[R_jO_2^{\cdot}] = CA_{kj}, \qquad (5)$$

where A_{kj} is the algebraic supplement to the element a_{kj} in the determinant of Eqns.(4). The constant C is determined from Eqns.(2) and (5):

$$C = \left[W_i \Big/ \left(\sum_{ij} k_{tij} A_{ki} A_{kj} \right) \right]^{1/2}. \qquad (6)$$

It can be determined analogously also for processes with linear and mixed chain termination.

The rate of consumption of each component is described by the expression[29]

$$\frac{d[R_iH]}{dt} = C \sum_j k_{pji} A_{kj} [R_iH]$$

and the overall rate of reaction is determined as the sum of the rates of consumption of all the components:

$$W = C \sum_{ij} k_{pij} A_{ki} [R_jH].$$

An important special case of a multicomponent system is a two-component system, which has been investigated in very many theoretical as well as experimental studies. The complete scheme for the initiated oxidation of the binary mixture at oxygen pressure sufficiently high to be able to neglect all the reactions of alkyl radicals apart from their interaction with oxygen can be formulated as follows:[27,28]

$$\begin{gathered} R_1H,\ R_2H \xrightarrow{W_i} R_1^{\cdot},\ R_2^{\cdot}, \\ R_1^{\cdot} + O_2 \rightarrow R_1OO^{\cdot}, \\ R_2^{\cdot} + O_2 \rightarrow R_2OO^{\cdot}, \\ R_1OO^{\cdot} + R_1H \xrightarrow{k_{p11}} R_1OOH + R_1^{\cdot}, \\ R_1OO^{\cdot} + R_2H \xrightarrow{k_{p12}} R_1OOH + R_2^{\cdot}, \\ R_2OO^{\cdot} + R_1H \xrightarrow{k_{p21}} R_2OOH + R_1^{\cdot}, \\ R_2OO^{\cdot} + R_2H \xrightarrow{k_{p22}} R_2OOH + R_2^{\cdot}, \\ \left.\begin{aligned} R_1OO^{\cdot} + R_1OO^{\cdot} &\xrightarrow{k_{t11}} \\ R_1OO^{\cdot} + R_2OO^{\cdot} &\xrightarrow{k_{t12}} \\ R_2OO^{\cdot} + R_2OO^{\cdot} &\xrightarrow{k_{t22}} \end{aligned}\right\} \text{inactive products.} \end{gathered} \qquad (7)$$

The equation for the overall rate of oxidation assumes the following form in this instance:

$$W = W_i^{1/2} \frac{r_1 [R_1H]^2 + 2[R_1H][R_2H] + r_2 [R_2H]^2}{\left(\frac{r_1^2}{a_1^2} [R_1H]^2 + 2\Phi \frac{r_1 r_2}{a_1 a_2} [R_1H][R_2H] + \frac{r_2^2}{a_2^2} [R_2H]^2 \right)^{1/2}}, \qquad (8)$$

where $r_i = k_{pii}/k_{pij}$, $a_i = k_{pii}/k_{tii}^{1/2}$, and $\Phi = k_{t12}/(k_{t11}k_{t22})^{1/}$ Analysis of this equation[30] made it possible to obtain an expression for the estimation of the effect of adding one of the components on the overall rate of oxidation and also on the rate of oxidation of each component. The form of the curve describing the dependence of the overall rate of reaction on the ratio of the concentrations of the mxiture components for variable kinetic parameters[30] and also on the absolute rate constants for chain termination in the oxidation of each component[31] has been analysed. The form of the curves describing the dependence of the overall rate of oxidation of a binary mixture and its individual components on composition has been investigated.[32-34]

The expression for the dependence of the rate of co-oxidation on composition can be simplified as follows.[34] The concentrations of the components will be expressed in terms of the volume fractions, i.e. $[R_1H] = [R_1H]_0(1 - x)$ and $[R_2H] = [R_2H]_0$, where x is the volume fraction of the second component and $[R_1H]_0$ and $[R_2H]_0$ are the molar concentrations of the components.

The boundary values of the derivatives of W with respect to x constitute a criterion which is a comparatively simple fucntion of the co-oxidation parameters and makes it possible to differentiate quantitatively various types of co-oxidation curves. Thus, for $x \rightarrow 0$, the expression for such a derivative is

$$\left(\frac{dW}{dx}\right)_{x \rightarrow 0} = W_i^{1/2} (2a_1 [R_2H]_0/r_1 - a_1 [R_1H]_0 - \Phi r_2 a_1^2 [R_2H]_0/r_1 a_2).$$

We shall consider three special cases which are possible for each of the boundary values of the derivatives, i.e. for derivatives corresponding to $x = 1$ and $x = 0$.

1. The slope of the tangent of the boundary point is zero, so that we have the straight lines AA_1 and BB_1 in Fig.1, i.e. the derivative is zero.

2. The direction of the tangent coincides with the line connecting the rates of oxidation of the individual components—a linear relation obtains.

3. The direction of the tangent coincides with the line describing the variation of the rate of oxidation of an individual component in an inert solvent and we have the lines AA_3 and BB_3 in Fig.1.

Having formulated and simplified the equations corresponding to each case, we obtain a set of expressions describing the relation between the co-oxidation parameters for the given boundary value of the derivative; they are written against the corresponding lines in Fig.1. Having denoted by the numerals 1–8 the sectors separated by these lines, we can divide all the co-oxidation curves into 16 types depending on the sector in which the parts of the curve corresponding to depleted mixtures are located.

Fig.2 presents certain types of such curves. A system of inequalities limiting the possible values of the co-oxidation parameters can be associated with each type of curve. The "greater than" and "less than" symbols defining the inequalities in a given sector are shown in Fig.1. For example, the following inequalities correspond to curves *1–5*:

$$r_2 < 2a_2/\Phi a_1;\ r_1 > 2a_1/a_2\Phi$$

and the inequalities

$$r_2 < 2a_2/\Phi a_1;\quad r_2 < 2a_2/\Phi a_1 - a_2^2 r_1/\Phi a_1^2;$$
$$r_2 < 2[R_1H]_0/[R_2H]_0 - \Phi a_2 r_1 [R_1H]_0/a_1 [R_2H]_0;$$
$$r_2 > 2a_2/a_1 - \Phi a_2^2 r_1/a_1^2$$

correspond to curves *2–7*.

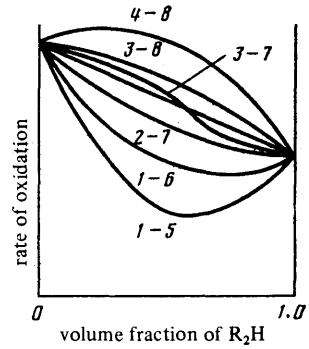

Figure 2. Types of co-oxidation curves.[34]

Using the given systems of inequalities and bearing in mind that only positive values of the parameters have a physical significance, it is possible to define rigorously the region in

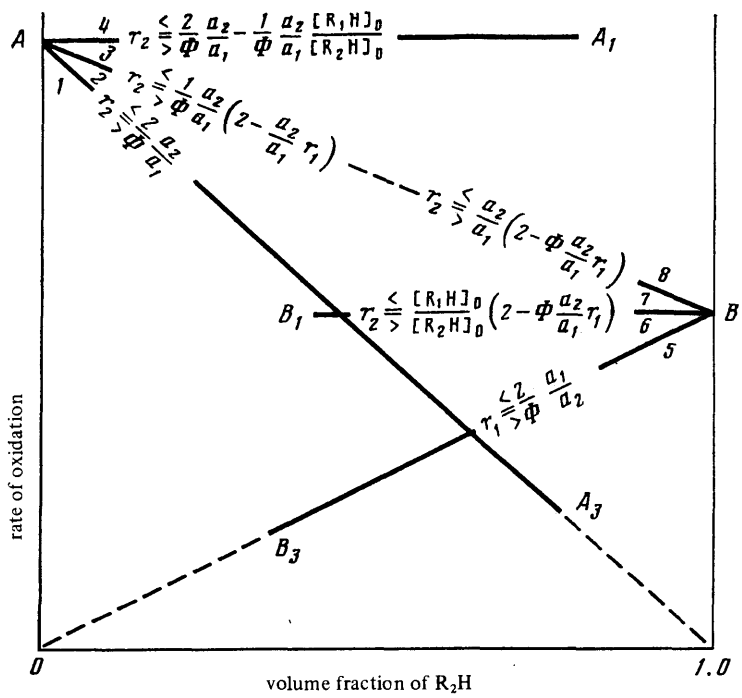

Figure 1. Equations relating the co-oxidation parameters for different boundary values of the derivative of the overall rate with respect to composition.[34]

which the co-oxidation parameters vary for each type of curve (Fig.3). As an example of the employment of the data in Fig.3, we shall analyse the problem of the type of co-oxidation parameters we should have for a system the dependence of the rate of oxidation of which on composition is described by a curve with a maximum, i.e. a curve of type *4–8*. The range of parameters *4–8* corresponds to this curve (Fig.3). Bearing in mind that all the relations presented in Fig.1 have been obtained for $a_1 > a_2$, one may conclude that an essential condition for a curve with a maximum is as follows: r_1 and r_2 should be small, not greater than 2. In practice this implies that the rate constants for the "cross" reactions k_{pij} should be comparable in magnitude or greater than the constants k_{pii}, i.e. the contribution of "cross" chain propagation reactions should predominate.

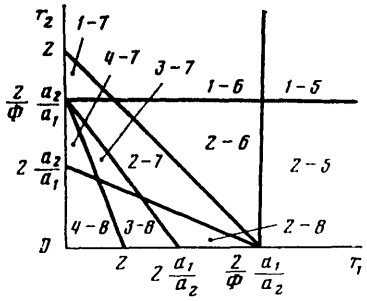

Figure 3. The ranges of the co-oxidation parameter for different types of curves.[34]

The inequalities obtained can be used also to solve the converse problem, which is of practical importance, namely the specification of the limits of the region in which the co-oxidation parameters are sought for a given type of co-oxidation curve by statistical analysis.

III. METHODS FOR THE DETERMINATION OF THE RATE CONSTANTS FOR ELEMENTARY REACTIONS IN CO-OXIDATION PROCESSES

The rate constants for the reactions of the radicals derived from one mixture component with the molecules of other components determine the specific features of the kinetics of the oxidation of the components of the mixture. In addition, they make it possible to compare the reactivities of many different molecules in reactions with the same radical and of a series of different radicals in reactions with the same molecule. At the present time there exist two methods for the determination of such constants. These are the Howard–Ingold method, based on the measurement of the rate of oxidation of one substance in the presence of the hydroperoxide of the other, and the joint oxidation method; we shall consider each of them.

1. The Howard–Ingold Method

A method has been proposed[35] for the determination of the rate constants for "cross" reactions based on the study of the kinetics of the oxidation of the hydrocarbon R_1H in the presence of the hydroperoxide R_2OOH. At high hdyroperoxide concentrations, the peroxy-radicals $R_1OO^\bullet$ and $R_2OO^\bullet$ are fully "exchanged" and the mechanism assumes the following form:

$$R_1H \rightarrow R_1^\bullet,$$
$$R_1^\bullet + O_2 \rightarrow R_1O_2^\bullet,$$
$$R_2OO^\bullet + R_1H \rightarrow R_2OOH + R_1^\bullet,$$
$$R_1OO^\bullet + R_2OOH \rightarrow R_1OOH + R_2OO^\bullet,$$
$$2R_2OO^\bullet \rightarrow \text{inactive products.}$$

The rate of reaction in this instance, subject to the condition that long chains obtain, is given by

$$W = \frac{k_{p21}}{k_{t22}^{1/2}} [R_1H] W_i^{1/2},$$

where k_{p21} and k_{t22} are the rate constants for the reactions of the peroxy-radicals formed from the hydroperoxide with the moelcules of R_1H and for quadratic chain termination respectively.

The applicability of this method has been demonstrated in relation to the oxidation of many organic substances—both hydrocarbons and their various derivatives substituted by functional groups.[36–42] However, on the basis of the results of their own study of the oxidation of tetralin in the presence of t-butyl hydroperoxide, Niki and Kamiya[43] cast doubt on the accuracy of the Howard–Ingold method. In reply to this criticism, Howard and Chenier[44] reinvestigated the same system and showed the need to ensure the complete "exchange" of the peroxy-radicals of the substance oxidised for the peroxy-radicals derived from the hydroperoxide and to make corrections for the evolution and absorption of gases in chain initiation and termination reactions.

However, the above factors are not the only ones which can significantly influence the validity of the values of the constants determined. When an attempt was made to apply this method to the determination of the rate constants for the reactions of cumenyl- and t-butyl-peroxy-radicals with polystyrene and adamantane at 348 K in solutions in chlorobenzene, results were obtained indicating a significant contribution of the chain decomposition reactions of the hydroperoxide to the given process.[45] Such decomposition, accompanied by the evolution of oxygen, leads to an unduly low measured rate of oxidation and hence introduces an error into the measured rate constant.

Thus, together with the undoubted advantages of the Howard–Ingold method, such as simplicity of the experiment and of the interpretation of the results, reliability of the results, particularly at low temperatures, and also the possibility of using it for substances with molecules having several reaction centres (the measured rate constant is then equal to the sum of the partial rate constants for the reactions of the hydroperoxy-radical with each of its centres), this method suffers from many disadvantages. The most significant of these are the rigorous requirements for the purification of the hydroperoxide and the difficulties arising from this in the determination of reproducible data, the possible complication of the process by the chain decomposition of hydroperoxides even at comparatively low temperatures (350 K), and the lack of availability of many hydroperoxides as a result of their lability.

2. The Co-oxidation Method

The method involving the joint oxidation of two substances for the determination of the co-oxidation parameters from which the rate constants for the "cross" reactions can be determined was developed much sooner than the Howard–Ingold method but the number of rate constants determined

with its aid is smaller because in many instances the accuracy of the value thus obtained is low. There exist several ways of determining the co-oxidation parameters from the results of the study of the kinetics of the co-oxidation of mixtures of two substances: (a) those based on the measurement of the consumption of the starting materials or the accumulation of each hydroperoxide; (b) those based on the measurement of the dependence of the overall rate of oxidation on the mixture composition.

The first group includes methods in which equations relating the ratio of the consumptions of the reactants (or the accumulations of the hydroperoxides) to the ratio of their concentrations in the mixture are employed:[46,47]

$$\frac{-\Delta[R_1H]}{-\Delta[R_2H]} = \frac{\Delta[R_1OOH]}{\Delta[R_2OOH]} = \frac{r_1[R_1H]/[R_2H]+1}{r_2[R_2H]/[R_1H]+1}, \qquad (9)$$

These methods have been used in a number of studies.[27,48-50] Their analysis, carried out by Niki et al.,[49] shows that small errors in the determination of concentrations lead to large errors in the determination of r_1 and r_2. Thus a 5% error in the measurement of [RH] leads to 10–30% errors in the calculated co-oxidation parameters.

The methods based on the use of Eqn.(9) are widely used for the determination of copolymerisation parameters. After the publication of the studies of Mayo and Lewis[46] and Fineman and Ross,[47] these methods were frequently modified in order to avoid their principal disadvantage, which is a marked dependence of the constants obtained on random experimental errors and also on the choice of coordinates in the linearisation of the plot of the dependence of the composition of the copolymer on the composition of the initial mixture.[51]

A significant fundamental limitation, which precludes in some cases the application of this group of methods to the determination of the co-oxidation parameters, should be noted: in order to measure the rate of consumption of a component or the rate of accumulation of the hydroperoxide with the required accuracy, one must carry out the reaction up to a significant degree of conversion: this leads to the accumulation of hydroperoxides in the system in amounts such that the contribution of their reactions

$$R_1OO^{\cdot} + R_2OOH \rightarrow R_1OOH + R_2OO^{\cdot},$$
$$R_2OO^{\cdot} + R_1OOH \rightarrow R_2OOH + R_1OO^{\cdot}$$

to the process becomes considerable. Analysis of the influence of the concentrations of the hydroperoxides formed on the accuracy of the parameters determined shows that even at concentrations of approximately 10^{-3} M the deviations can be significant.[34]

In the determination of the co-oxidation parameters from the dependence of the overall rate of oxidation on mixture composition, Eqn.(8) is employed. In the first study of this type[49,52-54] the following procedure was used: the system of non-linear equations containing three unknowns (r_1, r_2, Φ) is reduced to a system with two unknowns by eliminating one parameter on the basis of one of the equations; the resulting equations are solved in pairs by numerical or graphical methods. A disadvantage of this method is an unduly high statistical weight of one of the experiments and the consequent difficulty of a rigorous estimation of the accuracy of the parameters obtained.

Following the development of computers, it became possible to employ the methods of statistical analysis for the solution of this problem.[55,56] The accuracy of the estimates of the parameters is determined in this instance by the accuracy of the measurement of the rate of oxidation (it is usually fairly high) and also by the form of the co-oxidation curve. In particular, it has been shown[34] that, for a linear dependence of the rate of oxidation on mixture composition (and the volume fraction of the component), such a relation cannot be used to calculate the co-oxidation parameters. The latter are in this case related by equations of the type

$$r_2a_1/a_2 + \Phi r_1a_2/a_1 = 2,$$
$$r_1a_2/a_1 + \Phi r_2a_1/a_2 = 2,$$

which precludes the calculation of the unknowns r_1, r_2, and Φ, because there are only two equations. A partial solution is provided by the equation

$$\Phi = 1;\ 1/r_2 = r_1 = a_1/a_2.$$

A significant increase in the accuracy of the determination of the co-oxidation parameters can be achieved by a specific experimental design[56,57] which consists in the evaluation from preliminary estimates of the co-oxidation parameters of the ratio of the component concentrations for which the determinant of the information matrix has the maximum value; using the calculated ratio of the component concentrations, the next experiment is then performed and its results are employed in the recalculation of the co-oxidation parameters.

Table 1. Estimates of r_1, r_2, and Φ for the cumene–*o*-xylene system.[57]

No. of points	r_1	r_2	Φ
Uniform distribution of co-ordinates with respect to the composition axis			
6	1.76±0.52	0.638±0.030	1.34±0.48
12	1.27±0.22	0.658±0.017	0.99±0.26
Experimental design			
12	1.12±0.13	0.648±0.013	0.75±0.11

As an example, we present data obtained in the study of the co-oxidation of cumene and *o*-xylene[57] (Table 1). The data presented in Table 1 show that experimental design results in a considerable increase in the accuracy of the determination of all the co-oxidation parameters, particularly r_1 and Φ. The quantity r_2 for the given system (and for other systems of this type) is already determined with a satisfactory accuracy as a result of the first (non-optimal) measurements at six points distributed uniformly along the composition axis.

The literature data for the determination of the co-oxidation parameters from the dependence of the overall rate on composition show that this method, particularly when combined with statistical analysis and experimental design, ensures a satisfactory accuracy of the determination of the co-oxidation parameters. The existing experimental methods are fairly simple and permit the measurement of the quantities required for the calculation with a high accuracy. Another advantage of this method is that it makes it possible to obtain the parameters of the reactions also in cases where oxidation results in hydroperoxides which are unstable or difficult to isolate in a pure form.

Among the disadvantages of this method, one should include in the first place the dependence of the accuracy of the determination of the parameters on the form of the co-oxidation curve, which is why it cannot be applied to a whole series of systems. A significant limitation of the method can be in

many instances also the following factor. Studies of the oxidation of mixtures of substances whose molecules contain several C–H bonds with different energies have shown that the reaction kinetics are described satisfactorily by Eqn.(8). However, the kinetic parameters determined in this case are effective quantities and the expression for these include many constants for elementary reactions.[57–59]

We may also note that the effective rate constants for the chain termination reaction can be determined by the methods of non-stationary kinetics (the chemiluminescence[60] and interrupted illumination[61] methods) and in the case of a binary mixture they are described by the expression[62]

$$k_{t,\,\mathrm{eff}} = \frac{k_{t11}k_{p21}[\mathrm{R_1H}]^2 + 2k_{t12}k_{p21}k_{p12}[\mathrm{R_1H}][\mathrm{R_2H}] + k_{t22}k_{p12}^2[\mathrm{R_2H}]^2}{(k_{p21}[\mathrm{R_1H}] + k_{p12}[\mathrm{R_2H}])^2}.$$

For a multicomponent mixture, we have[63]

$$k_{t,\,\mathrm{eff}} = \frac{\sum_{ij} k_{tij}A_{ki}A_{kj}}{\left(\sum_i A_{ki}\right)^2}.$$

Table 2. The co-oxidation parameters of the cumene–R_2H systems.

No.	R_2H	T, K	r_1	r_2	Φ	Refs.
1	Ethylbenzene	333	0.5	0.8	1.3	[53]
	"	333	0.44	0.97	0.73	[64]
	"	333	1.3	1.0	1.2	[54]
	"	340.6	0.55	1.0	1.3	[65]
	"	348.5	0.59	1.0	1.2	[65]
	"	353	0.49	0.98	0.79	[64]
2	Tetralin	353	0.13	4.6	—	[48]
	"	353	0.21	5.0	4.3	[49]
	"	363	0.04	16	6	[66]
3	Toluene	333	3.0	0.2	0.8	[54]
	"	348	2.6	0.21	1.0	[57]
4	*p*-Xylene	333	2.1	1.0	2.1	[54]
	"	348	1.24	0.72	1.0	[57]
5	Mesitylene	333	2.2	0.8	1.1	[54]
	"	348	0.94	0.77	0.9	[57]
6	n-Propylbenzene	333	2.8	0.4	1.2	[54]
	"	348	1.4	0.72	1.0	[68]
7	n-Butylbenzene	333	1.9	0.9	1.2	[54]
8	Isobutylbenzene	348	3.5	0.10	1.0	[68]
9	s-Butylbenzene	348	2.0	0.30	0.8	[68]
10	Isopentylbenzene	348	2.3	0.50	4.6	[68]
11	Cyclopentylbenzene	333	0.1	4.0	—	[53]
12	Cyclohexylbenzene	333	0.55	0.75	0.75	[52]
	"	348	1.4	0.55	2.6	[68]
13	Neopentylbenzene	348	6.8	0.12	2.1	[68]
14	4-Methylpyridine	348	4.0	0.09	1.3	[70]
15	2-Methylpyridine	348	3.2	0.053	1.6	[70]
16	3-Methylpyridine	348	3.0	0.17	1.6	[70]
17	2-Isopropylpyridine	348	1.7	0.55	1.6	[70]
18	β-Bromoethylbenzene	348	1.6	1.4	1.0	[68]
19	*m*-Xylene	348	1.5	0.52	0.93	[57]
20	*o*-Xylene	348	1.12	0.65	0.8	[57]
21	Pseudocumene	348	0.63	1.24	0.9	[57]
22	2-Ethylpyridine	348	0.63	0.46	1.2	[70]
23	Diphenylmethane	348	0.42	2.2	1.4	[65]
24	Durene	348	0.32	2.12	0.9	[57]
25	4-Ethylpyridine	348	0.30	0.45	0.8	[70]
26	1,1-Diphenylethane	348	0.18	2.8	8.3	[69]
27	3-Ethylpyridine	348	0.17	0.69	0.64	[70]
28	Pentamethylbenzene	348	0.112	3.42	0.8	[57]
29	Hexamethylbenzene	348	0.087	8.83	1.0	[57]

by the simplest kinetic scheme corresponding to the mechanism with quadratic chain termination by peroxy-radicals and the oxidation takes place with fairly long chains.[1] The mechanism of the low-temperature oxidation reaction of mixtures of aromatic alkyl-substituted hydrocarbons is described by a simple kinetic scheme and it is therefore possible to calculate the kinetic co-oxidation parameters. At a quantitative level, i.e. with determination of the co-oxidation parameters, studies have now been made on more than 60 systems (Tables 2 and 3).

Table 3. The co-oxidation parameters for binary systems of aromatic alkyl-substituted hydrocarbons.

No.	R_1H	R_2H	T, K	r_1	r_2	Φ	Refs.
1	Tetralin	Mesitylene	333	6.5	0.15	1	[54]
2	Tetralin	n-Propylbenzene	333	6.7	0.1	1	[54]
3	Tetralin	*p*-Xylene	333	4.6	0.15	0.6	[54]
4	Tetralin	Pseudocumene	333	4.3	0.15	1.4	[54]
5	Tetralin	s-Butylbenzene	333	4.0	0.25	0.9	[54]
6	Tetralin	n-Butylbenzene	333	3.5	0.15	1.4	[54]
7	Tetralin	*o*-Xylene	333	3.1	0.15	0.6	[54]
8	Tetralin	Ethylbenzene	333	3.0	0.2	0.8	[54]
9	Tetralin	*m*-Xylene	333	2.6	0.1	0.6	[54]
10	Tetralin	Cymene	333	1.8	0.4	1.1	[54]
11	Ethylbenzene	Mesitylene	333	0.5	1.2	1.0	[54]
12	Ethylbenzene	*p*-Cymene	333	0.8	1.25	0.9	[54]
13	Ethylbenzene	n-Propylbenzene	333	1.0	0.8	1.0	[54]
14	Ethylbenzene	s-Butylbenzene	377	1.6	0.6	1.0	[54]
15	Ethylbenzene	n-Butylbenzene	377	0.8	1.2	1.2	[54]
16	Ethylbenzene	Neopentylbenzene	348	4.9	0.54	1.8	[71]
17	Ethylbenzene	Isobutylbenzene	348	2.5	0.35	1.0	[71]
18	Ethylbenzene	Toluene	348	2.2	0.2	3.0	[67]
19	Ethylbenzene	β-Bromoethylbenzene	348	1.8	0.25	0.9	[71]
20	Ethylbenzene	n-Hexylbenzene	348	1.8	0.62	1.4	[71]
21	Ethylbenzene	Diphenylmethane	348	0.31	1.2	2.5	[67]
22	Ethylbenzene	s-Butylbenzene	348	0.53	1.14	1.0	[71]
23	Ethylbenzene	Isopentylbenzene	348	0.7	0.7	2.0	[71]
24	Ethylbenzene	Cyclohexylbenzene	348	0.33	0.9	1.8	[71]
25	*o*-Xylene	*m*-Xylene	377	3.0	0.1	0.9	[54]
26	*o*-Xylene	*p*-Xylene	377	1.6	1.0	0.6	[54]
27	*m*-Xylene	*p*-Xylene	377	1.0	1.6	0.6	[54]
28	*o*-Xylene	n-Butylbenzene	377	0.5	1.8	1.1	[54]
29	Diphenylmethane	Toluene	348	6.3	0.10	3.0	[69]
30	1,1-Diphenylethane	Toluene	348	5.2	0.07	3.6	[69]
31	3-Isopropylpyridine	3-Methylpyridine	348	3.7	0.28	1.2	[72]
32	2-Isopropylpyridine	3-Methylpyridine	348	2.2	0.30	1.1	[72]
33	4-Isopropylpyridine	3-Methylpyridine	348	1.8	0.36	0.8	[72]
34	1,1-Diphenylethane	Diphenylmethane	348	1.3	0.51	3.2	[67]
35	s-Butylbenzene	n-Butylbenzene	377	0.3	2.0	1.1	[54]
36	*p*-Cymene	Toluene	333	2.2	0.4	1.0	[54]

Table 4. The parameters of the co-oxidation of aromatic alkyl-substituted hydrocarbons with alkanes.

R_1H	R_2H	T, K	r_1	r_2	Φ	Refs.
Tetralin	*cis*-Decalin	333	12	0.42	—	[48]
Pinane	Cyclohexylbenzene	333	2	0.4	0.4	[53]
Ethylbenzene	n-Decane	350	2.0	0.17	4.5	[55]
Ethylbenzene	2,7-Dimethyloctane	350	1.5	0.37	2.6	[55]
Pinane	Cyclopentylbenzene	333	0.9	1.7	4.0	[53]
Cumene	*cis*-Hexalin	333	0.58	1.56	—	[48]
Cumene	Decalin	333	0.5	0.27	1	[52]
Cumene	Pinane	333	0.4	0.7	4.0	[73]

IV. OXIDATION OF BINARY MIXTURES OF ORGANIC SUBSTANCES

The liquid-phase oxidation of aromatic alkyl-substituted hydrocarbons has been studied in greatest detail, which can be explained primarily by the fact that the kinetics of the oxidation reactions of such individual compounds are described

One of the most thoroughly investigated systems is the cumene–ethylbenzene system. The co-oxidation parameters for this system, measured in various investigations, agree well with one another (Table 2). The quantity Φ for the vast majority of systems is close to unity and its derivations from unity for some systems (see, for example, systems 10 and 12 in Table 2 and system 23 in Table 3) are probably

associated with the fact that in such cases Φ is an effective quantity, because the molecules of the substance undergoing co-oxidation in the presence of cumene always have several reaction centres. For systems 13 and 26 (Table 2) and 16, 18, 23, 24, 29, 30, and 34 (Table 3), the deviation of Φ from umity can be associated with the low accuracy of the determination of the co-oxidation parameters from the dependence of the overall rate of oxidation on composition, which is close to linearity for such systems.

The results of the study of the oxidation reactions of binary mixtures of aromatic alkyl-substituted hydrocarbons together with alkanes are presented in Table 4. Considerable deviations of Φ from unity are oobserved in these systems.

Table 5. The co-oxidation parameters for binary mixtures with oxygen-containing derivatives of hycrocarbons.

System	r_1	r_2	Φ	Refs.
Cumene-n-butyl ether	0.17	2.3	0.21	[74]
Cumene-isopropyl ether	0.11	2.2	0.55	[74]
Cumene-tetrahydrofuran	0.11	5.8	0.07	[74]
Cumene-2-methyltetrahydrofuran	0.11	17.5	0.5	[74]
Cumene-$(C_6H_5)(CH_3)(CH)_2O$	0.5	9.5	0.87	[74]
Tetralin-isopropyl ether	2.2	0.67	0.4	[74]
Tetralin-tetrahydrofuran	5.8	1.2	0.5	[74]
Tetralin-dibenzyl ether	0.7	2.4	2.6	[74]
Tetralin-benzyl ether	0.88	0.48	—	[48]
n-Butyl ether-isopropyl ether	0.65	1.6	1.7	[74]
Dibenzyl ether-$(C_6H_5)(CH_3)(CH)_2O$	4.3	0.45	0.3	[74]
Dibenzyl ether-2-methyltetrahydrofuran	2.5	0.48	1.2	[74]
Isopropyl ether-$(C_6H_5)(CH_3)(CH)_2O$	0.84	0.61	2.1	[74]
Tetrahydrofuran-methyltetrahydrofuran	0.56	1.6	0.8	[74]
1-Phenyl-1-propanol-cyclohexanol	1.8	0.43	0.7	[73]
1-Phenyl-1-propanol-2-butanol	1.1	0.34	1.44	[73]
1-Phenyl-1-propanol-tetralin	0.52	0.25	2.45	[73]
Cumene-cyclohexanone	0.2	0.4	—	[73]
Cumene-o-chlorobenzyl alcohol	0.97	2.2	6.5	[34]
Ethylbenzene-benzyl alcohol	0.80	2.3	0.7	[34]
Diphenylmethane-benzyl alcohol	0.26	8.0	0.7	[34]
Bibenzyl-benzyl alcohol	0.27	5.7	1.6	[34]
Cumene-n-butyl benzoate	2.6	0.08	1.1	[75]
Cumene-benzyl acetate	3.9	0.55	4.8	[75]
Cumene-benzyl butyrate	7.1	0.9	2.6	[75]
Cumene-2-heptylcyclohexanone	0.7	2.1	0.5	[76]

Studies have been made of systems comprising oxygen-containing derivatives of hydrocarbons (Table 5). One should note that, in the oxidation of ethers, the intraradical isomerisation reactions of the peroxy-radicals are significant.[4] Allowance for these reactions in the kinetics co-oxidation scheme leads to a relation between the rate of oxidation and mixture composition more complex than Eqn.(8). The co-oxidation parameters obtained using Eqn.(8) for systems containing ethers should therefore be regarded as effective quantities, i.e. as quantities incorporating the rate constants for both the intramolecular transport reaction and other elementary stages.

Eqn.(8) describes satisfactorily the dependence of the rate of oxidation of mixtures on composition for systems incorporating an aromatic alkyl-substituted hydrocarbon and an alcohol, ether, or ketone (systems 1–9 and 17–26 in Table 5), but the problem of whether or not the co-oxidation parameters are also effective quantities in this instance remains open. The point is that the determination of these parameters requires the alteration of the ratio of the hydrocarbon and the oxygen-containing derivative within very wide limits, which leads to considerable changes in the properties of the medium. The change in the properties of the medium can influence significantly the rate constants for the individual elementary stages[2] and the rate constants entering into Eqn.(8) may therefore prove not to be invariant over the entire range of concentrations of the components.

Apart from the systems presented in Table 5, studies have also been made of the kinetics of the co-oxidation of more than 50 binary mixtures of oxygen-containing compounds with polyhydric alcohols or esters in the range of compositions where the concentration of one component (R_1H) is much higher than that of the other (R_2H).[79] In this case the kinetic reaction scheme is simplified as a consequence of the low contribution of the $R_2OO^{\bullet} + R_2H$ and $R_2OO^{\bullet} + R_2OO^{\bullet}$ reactions, which makes it possible to determine experimentally the quantity α defined by the formula[79]

$$\alpha = 2\frac{k_{p12}}{k_{p11}} - \frac{1}{2}\frac{k_{t12}}{k_{t11}} \cdot \frac{k_{p12}}{k_{p21}}.$$

In many systems the second term is much smaller than the first, which enabled Degtyareva et al.[79] to estimate the quantities k_{p12}/k_{p11}, i.e. $1/r_1$. Thus $1/r_1$ for various alcohols in the n-hexadecane (R_1H)–alcohol (R_2H) systems has the following values respectively at 403 K: 2.8 for 1-decanol; 4.5 for 2-octanol; 2.2 for butane-1,3-diol; 12 for 1,1,1-tri-(hydroxymethyl)propane.

In the joint oxidation of aromatic alkyl-substituted hydrocarbons in alcohols, a sharp decrease of the rate of oxidation is observed following the addition of small amounts of an alcohol to the hdyrocarbon.[73,80] In relation to the cumene–benzyl alcohol system, it has been shown[81,82] that in this case the contribution of the reactions involving chain propagation by peroxy-radicals derived from the alcohol is negligible, which makes it possible to describe the dependence of the overall rate of oxidation W on the alcohol concentration $[R_2H]$ by the familiar[4] equation for inhibited oxidation:

$$\frac{W_0}{W} - \frac{W}{W_0} = 2\frac{k_{p12}}{(k_{t11}W_i)^{1/2}}[R_2H], \qquad (10)$$

where W_0 is the rate of oxidation of the hdyrocarbon without added alcohol. The same equation describes the kinetics of the co-oxidation of mixtures of hydrocarbons with amines.[83]

Binary systems containing aldehydes were the first systems in which co-oxidation has been investigated.[27] The parameters r_1 and r_2 for a number of systems have been determined from the kinetics of the accumulation of acids in the first hours of the co-oxidation reactions of substituted benzaldehydes (Table 6). Binary mixtures containing aldehydes and cyclohexadiene,[76] whose co-oxidation parameters have been determined using Eqn.(9), have also been investigated in detail.

A characteristic feature of the kinetics of the oxidation of mixtures incorporating aldehydes is a significant diminution of the rate of oxidation with time as a consequence of the formation in the course of the process of substances which probably possess inhibiting properties.[85,86] One of the general features of the kinetics of the oxidation of mixtures of aldehydes with organic substances of other classes is that the rate of reaction is strongly retarded not only by classical inhibitors but also virtually by all other substances with a mobile hydrogen atom or substances capable of undergoing addition reactions. Thus the oxidation of aldehydes is subjected to a powerful inhibiting effect by aromatic alkyl-substituted compounds,[76,84–86] olefins,[87–89] alcohols,[90,91] ketones,[92,93] and polycyclic hydrocarbons.[96] In some studies[86,95,96] it has been shown that the additive influences the rate of oxidation of the aldehyde via the usual mechanism of inhibited oxidation and canbe described by Eqn.(10). The kinetics of the oxidation of an aldehyde in the presence of a hydroperoxide can be described by the Howard–Ingold scheme

In the co-oxidation of two aldehydes one can observe an increase of the overall rate of oxidation of the mixture compared with the oxidation of the individual components,[77] which is associated with the increase of the rate of chain initiation in such mixtures. The maximum rate of chain initiation in the benzaldehyde–decanol mixture is attained for a 1 : 1 component ratio.

Table 6. The co-oxidation parameters for systems containing aldehydes.

System	T, K	r_1	r_2	Refs.
p-Chlorobenzaldehyde-*p*-methoxybenzaldehyde	303	0.15	2.36	[27]
p-Chlorobenzaldehyde-*p*-methylbenzaldehyde	303	0.24	2.15	[27]
p-Chlorobenzaldehyde-*m*-methylbenzaldehyde	303	0.33	2.20	[27]
p-Chlorobenzaldehyde-*p*-propylbenzaldehyde	303	0.28	1.87	[27]
p-Chlorobenzaldehyde-*p*-cyanobenzaldehyde	303	1.15	0.46	[27]
p-Chlorobenzaldehyde-benzaldehyde	303	0.54	1.62	[27]
m-Chlorobenzaldehyde-benzaldehyde	303	0.38	1.95	[27]
p-Methoxybenzaldehyde-benzaldehyde	303	2.22	1.0	[27]
p-Chlorobenzaldehyde-n-butyraldehyde	303	0.28	10.7	[27]
n-Heptanal-cyclohexadiene	273	0.64	1.65	[76]
n-Octanal-cyclohexadiene	273	0.64	1.65	[76]
n-Hexanal-cyclohexadiene	273	0.95	0.44	[76]
Pivaldehyde-cyclohexadiene	273	2.15	0.36	[76]
Benzaldehyde-cyclohexadiene	273	0.17	4.75	[76]
n-Heptanal-benzaldehyde	273	10	0.1	[76]
n-Decanal-benzaldehyde	273	8.6	0.2	[77]
Benzaldehyde-2-propanol	273	4	0.067	[78]
Benzaldehyde-benzyl alcohol	273	0.8	0.43	[78]

Table 7. The parameters of the co-oxidation of polystyrene with aromatic alkyl-substituted derivatives (348 K).[101]

System	r_1	r_2	Φ
PS-cumene	0.55	1.96	0.59
PS-diphenylmethane	0.62	1.25	1.21
PS-benzyl alcohol	0.72	20.3	2.64

Another important feature of the kinetics of the oxidation of binary mixtures containing an aldehyde is a considerable increase in the rate of oxidation of the second component, which is indicated by estimates of the rates from the co-oxidation parameters and by direct measurements.[76,79]

Data for the oxidation of mixtures of aldehydes with alkenes and also of alkenes with other substances have been examined in two studies[10,98] and are not presented in this review.

The joint oxidation of high-molecular-weight compounds in solutions and also their oxidation in mixtures with low-molecular-weight substances has so far been little studied. Only a few investigations[99,100] devoted to this problem are known. In the study of the co-oxidation reactions with participation of high-molecular-weight substances, difficulties due to the degradation of the polymers in the oxidation reaction and the influence of the co-oxidising component on the degradation arise compared with mixtures of low-molecular-weight substances (for which the principal object of study is the dependence of the rate of oxidation of the mixture and of the rates of oxidation of the individual components on composition).

It has been shown for the co-oxidation of cumene with polyethylene that the rate of degradation of the polymer diminishes linearly with increase of the concentration of cumene, although the rate of oxidation of the latter does not change in the presence of polyethylene.[99] The rate constant for the reaction of the cumenylperoxy-radical with polyethylene was determined in the same study. The rate of oxidation of cumene decreases appreciably with increase in the polystyrene content (PS) of the latter.[100] The dependence of the rate of oxidation of cumene on that of PS is described by a straight line in terms of the variables of the Eqn.(10), which enabled Guk et al.[100] to calculate the rate constant for the reaction of the cumenylperoxy-radical with PS.

For several systems, one of the components of which is polystyrene, the co-oxidation parameters have been determined (Table 7) from the overall dependence of the rate of oxidation on the composition of the binary mixture.[101] The calculation of the rate of oxidation of polystyrene in mixtures, carried out using the co-oxidation parameters obtained, showed that the addition of PS retards the oxidation of cumene and diphenylmethane but hardly influences the rate of oxidation of benzyl alcohol. Cumene and dimethylmethane in their turn accelerate the oxidation of PS, while benzyl alcohol inhibits this process. The addition of low-molecular-weight substances to a solution of polystyrene lowers the rate of its oxidative degradation.[102]

Different organic compounds have different effects on the degradation of PS in its oxidation in solution.[103] In terms of the magnitude of the inhibiting effect, they can be arranged in the sequence cumene < toluene < esters < cumenyl hydroperoxide < benzyl alcohol.

Shilov and Denisov[104] compared the relations between the rate of oxidation and composition in systems consisting of polyethylene, polypropylene, and their low-molecular-analogues—n-decane and 2,2,4-trimethylpentane respectively. In the co-oxidation of low-molecular-weight hydrocarbons a curve with a hump (of type 3–7 in Fig.2) is observed. For the polyethylene–polypropylene system, the rate of oxidation varies linearly with the composition of polymers, which has been explained[104,105] by the absence of cross-reactions in the given systems, i.e. the chain oxidation develops within each individual molecular coil.

Thus hitherto detailed studies have been made on the joint oxidation reactions of mixtures of aromatic alkyl-substituted compounds, alkanes, alkenes, alcohols, ketones, aldehydes, polyolefins, ethers, and esters. The reactions involving individual representatives of other classes have also been investigated. Thus, among chloro-derivatives, a study has been made of the joint oxidation reaction of benzyl chloride and cumene;[106] the overall rate of oxidation is found to decrease both after the addition of cumene to benzyl chloride and after the addition of benzyl chloride to cumene, i.e. the co-oxidation curve is of type *1–5*.

The kinetics of the co-oxidation of cumene in the presence of a series of amines have been investigated.[83,107] A characteristic feature of the kinetics of these processes is that small amounts of added amine diminish partly the overall rate of oxidation.

All the curves quoted in the literature for the dependence of the rate of reaction on the mixture composition are combined in Table 8 in six groups each of which includes several types (Fig.1).

The data in Table 8 show that, among the 164 systems investigated, only one is described by a curve with a maximum. Unfortunately the authors[74] do not quote the curve, stating only the co-oxidation parameters, the accuracy of the determination of which is insufficient to regard the conclusion concerning the shape of the curve as rigorously unambiguous.

Only approximately 7% of all the systems investigated exhibit small positive deviations from linearity, i.e. in these systems the rate of oxidation of the mixture is somewhat greater than the sum of the rates of oxidation of its components taken at the same concentrations in an inert solvent. Among the systems whose rate of oxidation varies with composition in accordance with a linear law, the majority are those in which the molecules of the components have similar chemical structures.

Table 8. The numbers of systems investigated described by different types of co-oxidation curves.

Composition-rate relation	Type of curve	Number of systems
Linear		35
With a maximum	*4—8*	1
With positive deviations	*3—8*	10
With negative deviations	*1—7, 2—7*	81
With a minimum	*2—6, 2—5*	35
With inflections	*1—8, 2—8, 3—5, 3—7*	2

Table 8 shows that the most characteristic feature established in the study of the kinetics of the co-oxidation of binary systems is a decrease of the overall rate of oxidation of the mixture compared with additivity, i.e. negative deviations from linearity.

The systems of inequalities which limit the values of the co-oxidation parameters are presented above in Table 1. However, they are too complex for practical analysis. In order to analyse the problem of what should be the relations between the parameters for a particular type of curve, the concept of reaction selectivity is employed.[108] We shall define the selectivities in the interaction of the reacting species in co-oxidation processes in the following manner.

1. The selectivity of the reactions of a molecule with two peroxy-radicals:

$$R_iOO^{\cdot} + R_nH \xrightarrow{k_{pin}} R_iOOH + R_n^{\cdot},$$
$$R_jOO^{\cdot} + R_nH \xrightarrow{k_{pjn}} R_jOOH + R_n^{\cdot},$$
$$S_{M_n/R_iR_j} = k_{pin}/k_{pjn};\ k_{pin} > k_{pjn}.$$

2. The selectivity of the reaction of a radical with molecules:

$$R_nO_2^{\cdot} + R_iH \xrightarrow{k_{pni}} R_nO_2H + R_i^{\cdot},$$
$$R_nO_2^{\cdot} + R_jH \xrightarrow{k_{pnj}} R_nO_2H + R_j^{\cdot},$$
$$S_{R_n/M_iM_j} = yk_{pni}/xk_{pnj};\ yk_{pni} > xk_{pnj},$$

where x and y are the numbers of equivalent atoms in the R_iH and R_jH molecules respectively.

3. The selectivity of the reaction with radicals:

$$\left.\begin{aligned} R_nO_2^{\cdot} + R_iO_2^{\cdot} &\xrightarrow{k_{tni}} \\ R_nO_2^{\cdot} + R_jO_2^{\cdot} &\xrightarrow{k_{tnj}} \end{aligned}\right\} \text{molecular products};$$
$$S_{R_n/R_iR_j} = k_{tni}/k_{tnj};\ k_{tni} > k_{tnj}.$$

For two-component mixtures, the quantities i, j, and n assume values of 1 and 2.

Using this notation, the condition for linearity can be formulated as the following equality:[34]

$$\frac{S_{R_1/R_1R_2}}{S_{M_1/R_1R_2}} + \frac{S_{M_2/R_1R_2}}{S_{R_2/R_1R_2}} = 2.$$

This equation holds in particular when the selectivities for all the species are equal, i.e. are independent of the reactivity.

The following inequality corresponds to the most general case, namely negative deviations from additivity:

$$\frac{S_{R_1/R_1R_2}}{S_{M_1/R_1R_2}} + \frac{S_{M_2/R_1R_2}}{S_{R_2/R_1R_2}} > 2. \qquad (11)$$

For many systems, the availability of experimental co-oxidation parameters and rate constants for the individual elementary reactions permits the calculation of the selectivities in formula (11). The results of such calculations make it possible to conclude that in systems containing hydrocarbons, alcohols, ethers, esters, and chloro-derivatives, the decrease of the rate of co-oxidation is caused by the higher selectivity of the reactions of peroxy-radicals compared with the reactions of molecules. In systems with aldehydes the decrease in the rate of oxidation is caused by the higher selectivity of the reactions of molecules. Analysis shows that, when the selectivity of the reactions of species depends appreciably on the reactivity (it is then unimportant whether the selectivity increases or diminishes with increasing reactivity), inequality (11) holds. The general relations governing the dependence of the selectivity on the reactivity of the reacting radicals and molecules under the conditions of a wide variation of their structures have not so far been established. It has been shown only for reactions of certain peroxy-radicals with the molecules of aromatic alkyl-substituted compounds that the selectivity of the radical changes in parallel with reactivity.[34] This is indicated by two facts.

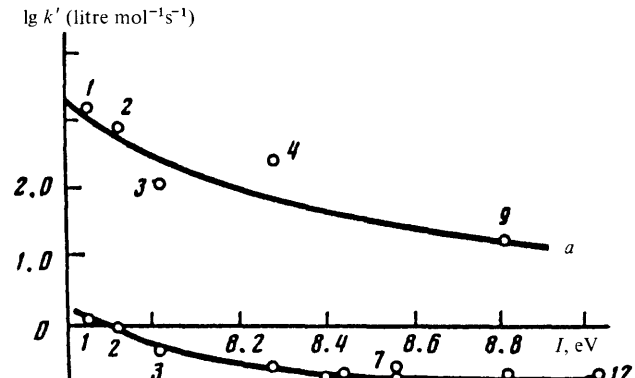

Figure 4. Dependence on the ionisation potentials of the molecules I of the partial rate constants k' for the reactions of the benzoylperoxy-radicals (a) and cumenylperoxy-radicals (b) with different substances: 1) hexamethylbenzene; 2) pentamethylbenzene; 3) durene; 4) pseudocumene; 5) mesitylene; 6) p-xylene; 7) o-xylene; 8) m-xylene; 9) toluene; 10)–12) picolines.[110]

Fig. 4 presents the variation of the partial (referred to a single reactive C–H bond) rate constants for the reactions of cumenyl peroxy- and benzoylperoxy-radicals with methyl-substituted benzene derivatives. It is seen that, with increased number of methyl groups in the ring, the partial rate constants also increase. The increase is more significant

for reactions of these molecules with the benzoylperoxy-radical, which is much more reactive than the cumenylperoxy-radical. This implies that the selectivity of the reaction of the more reactive radical, which is in this instance the benzoylperoxy-radical, is higher than the selectivity of the reaction involving the less reactive cumenylperoxy-radical.

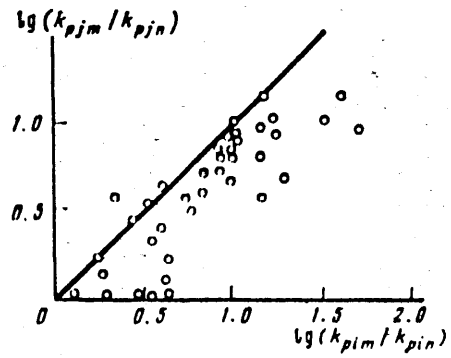

Figure 5. Relation between the selectivities of the reactions of peroxy-radicals; i is a more reactive radical than j; m is a more reactive molecule than n.[34]

The relation between the selectivities and reactivities of various peroxy-radicals can be traced also in terms of the co-oxidation parameters r_1 and r_2, which constitute the ratios of the rate constants for the reactions of two different peroxy-radicals for the same pair of molecules. We shall select from the binary systems investigated (Tables 2 and 3) those in which the oxidation of their components results in the formation of primary and tertiary, primary and secondary, or secondary and tertiary peroxy-radicals respectively. In order to determine which radical in the given pair is more reactive one can then employ the familiar reactivities in the series: primary > secondary > tertiary. The logarithm of the ratio of the rate constants for the reactions of the same pair of molecules with a less reactive radical is plotted in Fig. 5 against the logarithm of the ratio of the partial rate constants for the more reactive radical. Evidently most of the points lie below the line whose slope is unity, which demonstrates the greater selectivity of the reaction with the more reactive peroxy-radical.

V. THE SELECTIVITY OF THE REACTIONS OF THE COMPONENTS IN CO-OXIDATION

Using the approach developed by Emanuel'[109] for the estimation of the selectivities of liquid-oxidation reactions, we shall consider in greater detail the problem of the influence of the reactivity of the component on the rate and selectivity of the oxidation in mixtures.

In order to establish a relation between the co-oxidation parameters and the shape of the curve describing the dependence of the rate of oxidation of the individual components on the mixture composition, we shall make use of the limiting values of the derivative of the rate of oxidation of the component W with respect to its volume fraction in solution x for $x \to 0$ or $x \to 1$.

The systems of inequalities relating the kinetic co-oxidation parameters of various types of curves describing the rates of oxidation of the individual components are presented in Fig. 6. For example, the rate of oxidation of the second component in the region of mixtures enriched in the latter is higher than the rate of its oxidation in an inert solvent at the same concentration, provided that the following inequality holds: $r_1 < a_1/\Phi a_2$; in depleted mixtures the validity of the inequality $r_1 < a_1/a_2$ is sufficient for this purpose.

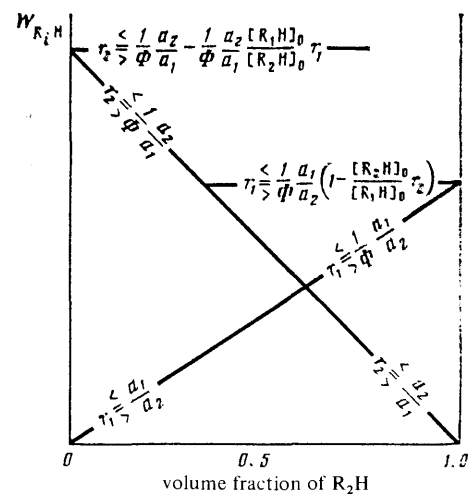

Figure 6. Equations relating the co-oxidation parameters for different derivatives of the rate of oxidation of the components with respect to composition.

The relations obtained[72] between the rate of oxidation of toluene and picoline (both these substances are relatively unreactive in liquid-phase oxidation reactions) and the composition of their mixture with cumene, whose reactivity is much higher, are presented in Fig. 7. These binary systems have been studied experimentally and their co-oxidation parameters have been obtained. Fig. 7 shows that a considerable increase of the rate of oxidation of the individual substances can be achieved in the co-oxidation reaction.

While the selectivity of the oxidation of an individual substance depends solely on the oxidation chain length and always diminishes when the substance is diluted by an inert solvent, the selectivity of the oxidation of the substance in the mixture is a complex function of the kinetic parameters and the concentrations of the components. In the simplest case of the oxidation of a mixture of two substances and subject to the condition $\Phi = 1$, the variation of the selectivity S_1 of the oxidation of the components R_1H and R_1OOH with composition is described by the expression[34]

$$\frac{1}{S_1} = 1 + \frac{(W_i k_{t11})^{1/2}}{k_{p11}[R_1H]_0 - (k_{p11}[R_1H]_0 - k_{p12}[R_2H]_0)\,x},$$

where $[R_1H]_0$ and $[R_2H]_0$ are the concentrations of the pure components and x is the volume fraction of the component R_2H. It follows from this equation that, in order to increase

the selectivity of the oxidation of a substance, it is necessary to add to it a second substance more reactive with respect to the peroxy-radicals $R_1OO^{\bullet}$.

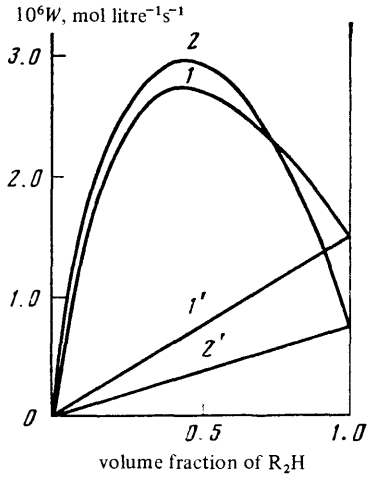

Figure 7. Dependence of the rates of oxidation of toluene (curves *1* and *1'*) and picoline (curves *2* and *2'*) on the composition of their mixtures with an inert solvent (curves *1* and *2*) and cumene (curves *1'* and *2'*) at 348 K.[72]

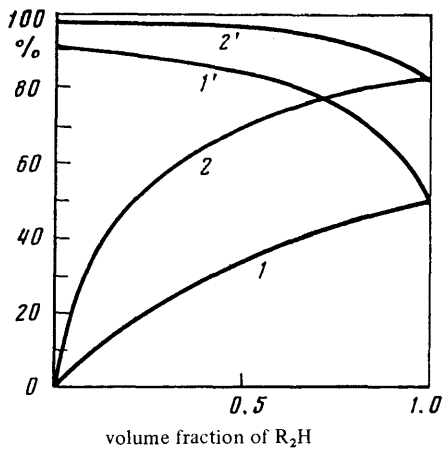

Figure 8. Dependence of the selectivity of the oxidation of the component R_2H on its content in a mixture with an inert solvent (curves *1* and *2*) and with the substance R_1H undergoing co-oxidation; $r_2 = 0.1$ (curves *1'* and *2'*) for different lengths ν of the oxidation chain: $\nu = 1$ (curves *1* and *1'*) and $\nu = 5$ (curves *2* and *2'*).

As an example, we calculated the dependence of the selectivity of the oxidation of the component R_2H in its mixture with a more reactive substance on the mixture composition for two oxidation chain lengths, namely 1 and 5; for clarity, short chains have been selected. The data presented in Fig. 8 show that, in contrast to the decrease of the selectivity on dilution of the substance R_2H by an inert solvent, the addition to R_2H of a more reactive substance entails an appreciable increase of the selectivity. For a chain length of unity, the selectivity of the oxidation of the pure substance is only 50%; on the other hand, in mixtures with a low content of this substance, the selectivity of its oxidation reaches as much as 90%. The selectivity of the oxidation of the second component also increases greatly for a chain length of 5 (from 83 to 98%).

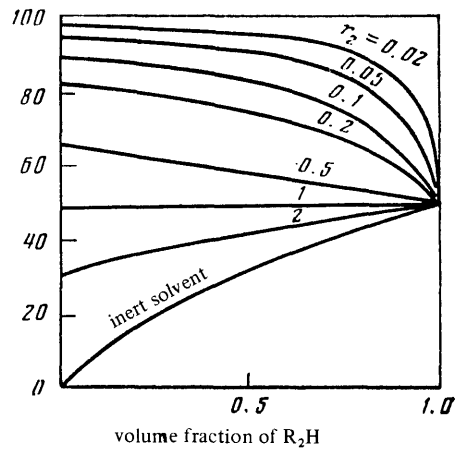

Figure 9. Dependence of the selectivity of the oxidation of the component R_2H on its content in a mixture with components R_1H having different reactivities.

In selecting the second mixture component, introduced in order to increase the selectivity of the oxidation of the required substance, its relative reactivity (relative to the given substance) is significant. The relations between the selectivity of the oxidation of the component R_1H and the mixture composition for different relative reactivities of the substance R_2H (this corresponds to different values of r_1) are presented in Fig. 9. Evidently, with increased reactivity of the second substance R_2H (a decrease of r_1 corresponds to this case), the selectivity of the oxidation of the first substance R_1H increases appreciably. Thus, in a mixture containing only 10 vol.% of a substance much more reactive than R_1H, the selectivity of the oxidation of the latter increases from 50 to 86%.[34]

The calculations and conclusions described above refer to reactions occurring under the conditions of initiated oxidation without degenerate chain branching. However, the results can be extended also to processes involving a mechanism with degenerate chain branching, provided that their main oxidation products are formed via the corresponding hydroperoxides.

Thus the oxidation of α-heptylcyclohexanone has been investigated[111] both separately and in mixtures with cumene. The results of kinetic studies showed that in co-oxidation the selectivity of the conversion of the ketone into an acid reaches 97%, while in the oxidation of the pure ketone it amounts to only 74% under the same conditions.

Thus in the oxidation of mixtures of substances with different reactivities a general feature is an increase of the selectivity of the conversion of the substance with the lowest

reactivity into hydroperoxides and products formed from the hydroperoxides in subsequent reactions.

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The data presented above permit the conclusion that the problems of describing the kinetics of unbranched chain oxidation reactions of organic substances under various conditions have been virtually solved. The examination and comparison of the available literature data for the kinetics of the co-oxidation of binary mixtures at low temperatures and high oxygen pressures showed that the principal feature of the dependence of the rate of oxidation of mixtures on composition is negative deviations of the rate of co-oxidation from additive values. The main cause of the appreciable negative deviations (observed in the oxidation of mixtures containing substances belonging to the classes investigated, with the exception of aldehydes) is a higher selectivity of the reactions of the peroxy-radical than that of the reactions of the initial molecule with peroxy-radicals formed in the given process. This can be used to select compositions which are difficult to oxidise.

Joint oxidation can serve as an effective means of regulating both the rate and selectivity of the oxidation of substances which are difficult to oxidise and can also be used to involve in the oxidation process substances which are hardly oxidised in a pure form under the given conditions.

In theoretical terms, the development of new experimental methods for the determination of the rate constants for various elementary liquid-phase oxidation cross-reactions is of interst. The co-oxidation method can be useful in the development of a procedure for the simultaneous synthesis of several chain products, which can be more economical than the synthesis of each of them separately. A more rigorous assessment of the likely usefulness of this method will become possible after the determination of the characteristic features of the kinetics of the joint oxidation at advanced stages of the process.

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The Modelling of Biological Catalysts

A.P.Purmal' and L.A.Nikolaev

A historical survey of studies on the modelling of biological catalysts is presented. Pioneering investigations, investigations which have led to new concepts, hypotheses, or principles, or those which have led to results of practical importance are examined. Attention has been concentrated on the modelling of oxidoreductases.
The bibliography includes 124 references.

CONTENTS

I. The first models of metalloenzymes 466
II. Metal complexes as models of active groups 467
III. Models of metal-free active groups of enzymes 468
IV. Metal complexes as models of catalase and nitrogenase 468
V. Models of oxidases, oxygenases, and other enzymes 470
VI. The modelling of enzymes as a pathway to new catalysts 471
VII. The role of the macromolecular component in model systems and of the protein in enzymes 472

Biological catalysts (enzymes) are specific protein catalysts present in all living cells. The study of non-protein catalysts, which accelerate the same reactions as enzymes, has been established as a field of research into the modelling of biological catalysts.

Any model reflects a particular characteristic feature of the original. If a high catalytic activity is regarded as the characteristic feature of enzymes, then colloidal solutions of metals must be regarded as the first models. Investigation of these systems dates back to the beginning of this century; the first object modelled among enzymes was catalase, which catalyses the decomposition of hydrogen peroxide under the conditions of the living cell.

I. THE FIRST MODELS OF METALLOENZYMES

Bredig and his co-workers investigated colloidal solutions of platinum and other highly dispersed noble metals and showed that these simple "models" do indeed resemble enzymes.[1,2] The study of the kinetics of catalytic processes in the presence of highly dispersed metals led to the observation of definite similarities between the kinetic characteristics of the models and the originals. Like enzymes, Bredig's models acted at very low concentrations and the dependence of the rate on the hydrogen peroxide concentration in the model systems was extremely similar to that characteristic of enzymes. This was observed not only for colloidal metals but also for metal oxide sols. The situation was the same for the influence of the pH on the catalytic activity; it was found to be similar in the model and modelled systems. An increase of the pH in both cases led to the attainment of a maximum in the rate of decomposition of the peroxide. The maintenance of solutions at elevated temperatures resulted in a decrease of the activities of both catalase and the model systems.

Comparison of the activities of specific substances (catalyst poisons) on enzymes and models is especially convincing. It was found that the models, i.e. metal sols, are inactivated by the same substances as catalase, namely by mercury compounds, cyanides, hydrogen sulphide, iodine, etc. After poisoning the platinum sol with hydrogen cyanide, the activity of the sol can be restored by the prolonged passage of air through the solution; catalase behaves in exactly the same way. Such high similarity in the dependence of various factors was to some extent due to the fact that the modelled enzyme contained a metal (iron) as part of the composition of the active group.

Metal salts have attracted the attention of many investigators,[3,4] but on the whole comparative study of the properties of sols and enzymes in fairly primitive systems has not been able to accelerate significantly progress in the modelling of biocatalysis.

It has been established[5,6] that platinum metals accelerate the decomposition of formic acid and also decompose formaldehyde (into CO and H_2). These may be seen as functions resembling the activity of oxidoreductases. The transfer of hydrogen from formaldehyde to Methylene Blue under the influence of the "Schardinger" enzyme from raw milk is modelled, according to Bredig and Sommer,[7] by the reduction of the dye with formic acid in the presence of platinum, iridium, gold, and palladium sols. For these reactions, it has been possible to demonstrate kinetic analogies with enzymes and to establish that enzyme poisons such as hydrocyanic acid and mercury salts have a poisoning effect.

In terms of activity, the sols are greatly inferior to enzymes. Thus, according to Hennichs' data,[8] a preparation of catalase from the liver is almost a thousand times more active than colloidal platinum. Admittedly, it is fairly difficult to carry out a comparison since neither their number nor the character of the distribution of the active centres on the sol particles nor the legitimacy of applying homogeneous kinetics to the microheterogeneous systems investigated are known.

There was a tendency to explain the catalysis by dispersed metals of the hydrogen peroxide decomposition reactions by the formation of intermediate peroxide compounds. Mercury peroxide compounds have been detected in the catalytic decomposition of H_2O_2 by mercury.[9]

Later studies of metal salts were concerned with the properties of tungsten,[10] colloidal silver,[11] and iron(III) hydroxide.[12]

Platinum metal salts are very unstable and their employment for preparative purposes would require an increase in their stability. This has been achieved by introducing into the colloidal metal solution the so-called protective colloids,

forming on the surface of the sol particles an adsorption layer which prevents their coagulation.[13,14] The products of the alkaline hydrolysis of egg albumin, namely the sodium salts of lysalbinic and protalbinic acids, were used as the protective colloid in 1904.[13] These acids are precipitated in an acid medium and they can be used only in neutral or weakly alkaline solutions. Using gum arabic as the protective colloid, active salts suitable for the hydrogenation of a large number of compounds over a wide pH range were obtained in 1912.[14]

Despite serious doubts about the usefulness of attempts to understand the mechanism of enzyme action by studying metal salts, careful investigation of this historical stage in the development of the science of catalysis has shown that it was by no means fruitless. If not the metals themselves then metal ions do indeed have a direct bearing on enzymes.

Progress in biological research, which had led to the discovery of the chemical nature of the active groups in metal-containing enzymes, has attracted attention to the catalytic properties of a surprising group of compounds containing a porphyrin nucleus and different metal ions coordinated to the system of pyrrole rings of the nucleus.

In 1926 the first step was taken in the study of the activities of groups characteristic of enzymes. Kuhn and Brann[15] investigated the catalytic activity of haemin—a complex of iron and a protoporphyrin ring. Compounds of this type constitute the active groups in many enzymes catalysing oxidation processes and the problem of the properties of haemin was therefore important from the standpoint of modelling. In enzymes, haemin is linked to the protein and measurement of the activity of isolated haemins threw some light on the role of the protein moieties of the molecules of biological catalysts (see Nikolaev's review[16]).

These experiments demonstrated particularly clearly that the active group, separated from its carrier, has a much lower activity and an extremely weak selectivity. The activity of haemin in the hydrogen peroxide decomposition reaction was increased by its adsorption on charcoal.[17] The adsorption activates haemin in relation to specific but by no means all the reactions in which it behaves in general as a catalyst.

Iron ions are also activated by adsorption on charcoal.[17] Such systems can be regarded as the simplest and very rough models of enzymes in which the active group and the carrier are already clearly outlined. At the same time it was shown that compounds which do not contain any metal and have a comparatively simple structure are capable of catalysing reactions characteristic of enzymes. Thus Shilov, who developed the concept of the cyclic transition complex in organic reactions,[18] studied the catalytic functions of amines and aminoacids;[19] Swain and Brown[20] showed that the catalytic effect can be determined by the simultaneous action on the substrate of two different functional groups contained in the catalyst molecule. This effect ("bifunctional catalysis") was subsequently shown to play an important role in the mechanism of enzyme action.

In the subsequent research into the modelling of enzymes, two trends were established: (1) the study of models of the active groups of enzymes in order to elucidate the characteristics of the structure and mechanism of their action as part of the composition of the enzyme; (2) the synthesis of highly active catalysts based on the existing information about the structure and specific mechanism of enzyme action.

The first of these trends outgrew in the course of its development the initial aims of the investigations and led to the formulation of a new branch of chemistry—metal complex catalysis. In our country, studies on these lines were initiated by one of the authors of this review.[21]

II. METAL COMPLEXES AS MODELS OF ACTIVE GROUPS

Nikolaev[16,22,23] carried out a series of investigations of models of the active groups of metal-containing enzymes and chose copper as the model metal. In contrast to the ions of iron, whose hydroxide $Fe(OH)_3$ has a very low solubility product, copper ions form many complexes which are stable in an aqueous medium in the presence of an excess of the ligand in solution and permit a wider variation of the nature of the ligands. Other metal ions were later also studied as catalysts of various reactions (decomposition of hydrogen peroxide, oxidation of polyphenols, oxidation of ascorbic acid, etc.) and the first relations between the catalytic activity and the nature of the ligand were formulated.

The results obtained are summarised in a monograph[16] and reviews.[22,23] The main idea, which stimulated the study of the catalytic properties of complexes, consisted in the hypothesis that the properties of the active centre in heterogeneous catalysts can be interpreted in terms of data concerning the influence of the environment of the metal ion on its activity and the complex is to some extent an analogue of the active centre "extracted" from the solid and transferred to the solution. This way of "creating bridges" between heterogeneous and homogeneous catalysis has since become promising, but progress along this pathway requires more effort than seemed to be the case at the beginning. Nevertheless, even the first steps have already shown that the variation of the activity and selectivity of catalysts of the type of metal complexes is entirely feasible and leads to extensive and interesting trends in the theory and practice of catalysis. The study of the influence of the nature of ligands, the nature of the metal ion, and the geometrical characteristics of metal complexes threw light on many aspects of the mechanism of enzyme action and clarified the problems which must be solved in theoretical enzymology.

In the first place it was found that the condition which must be fulfilled for the complex to exhibit an appreciable catalytic activity at all is the limitation imposed on the coordination number, namely the latter must not be greater than four. Complexes of the "closed" type with a coordination number of six or more are as a rule inactive.

The presence in the coordination sphere of amine nitrogen is also important for metal complex catalysts of redox processes and in particular of the decomposition of hydrogen peroxide—the introduction of oxygen into this sphere lowers the activity. American investigators[24] have shown that these conditions are to a large extent valid also in the catalysis of the hydrolytic reactions of organic substances by transition metal complexes.

The investigation of the catalytic properties of the iron complex of triethylenetetramine, which has come to be called "inorganic catalase", belongs to this series of investigations.[25,26] As in the early studies by Bredig, these investigations emphasise the similarity in the nature of the catalytic poisons of catalase and the complex investigated and also the similar isotope effects. Among all the metal complexes investigated hitherto, this system has shown the highest catalase activity (subject to the same stipulations concerning the difficulty of the correct comparison of the catalytic activities of systems in terms of their turnover number determined at different pH). It was later shown[27] that the complexes of iron ions with triethylenetetramine model an important feature of the catalase process. The mechanism of the catalysis of the decomposition of hydrogen peroxide by this complex involves a sequence of two two-electron transfers, i.e. the catalysis has a non-radical mechanism as in the case of catalase.

The properties of metal sols containing on their surfaces compounds of different composition, have been described from the standpoint of catalysis and colloid chemistry.[28] Micellar catalysis, which can be regarded as one of the aspects of the modelling of biological catalysts, should be treated as a further development of this trend.

A review of metal complexes in which the ligand is a molecule or ion of the substrate can be found in a monograph.[29]

III. MODELS OF METAL-FREE ACTIVE GROUPS OF ENZYMES

Investigations into model structures without metal ions developed in parallel with the studies devoted to the metal complex models of the active groups of enzymes. Researches into the latter led to the establishment of a new field of science—that of metal complex catalysis. Studies on the former compounds laid specific foundations for another branch of science—catalysis by organic compounds.

The possibility of creating simple organic models of enzymes was foreseen in an early stage by Ostwald[1] (p.161). The first attempts to demonstrate the similarity of the stereochemical specificities of enzymes and simple organic models were undertaken in 1908. It was shown that nicotine resolves the optical isomers of camphorcarboxylic acid at different rates[1] (p.161).

In 1927 Langenbeck investigated isatin as a model of the enzyme dehydrase and established the mechanism of its action, which has features in common with the mechanism of the enzyme action.[30] Three years later Langenbeck, Hutschenreuter, and Jütteman proposed the principle of systematic activation[1] (p.96). A number of rules were formulated whereby one could be guided whilst modifying in succession a simple organic compound, chosen as the model of the enzyme, in order to increase its catalytic activity.

A striking demonstration of the effectiveness of the principle of systematic activation is provided by the study of methylamine and its derivatives as catalysts of the decarboxylation of phenylglyoxylic acid. By successive modification of methylamine to form 3-amino-1-methyloxindole, it has been possible to increase its decarboxylase activity a thousandfold. Using this procedure, investigators approached the elucidation of the structure of the active group in decarboxylase. The results of studies by Braunstein and Shemykin[31] and by Metzler and co-workers[32-34] constituted a major advance in the employment of the modelling method in order to establish the mechanism of enzyme action. These studies were concerned with the investigation of the models of transaminases and other pyridoxal transamination, racemisation, etc. enzymes. Pyridoxal or its phosphate, i.e. a relatively simple organic compound without its protein component, served as the model system.

It is necessary to consider studies which led to the elucidation of the activating role of the macromolecular component linked to the model of the active group of the enzyme. The activation of haemin and iron ions by their adsorption on charcoal has already been mentioned above. Model systems of this kind without metal ions were described in 1932 and were called faser-catalysts.[2] Faser-catalysts are derivatives of cellulose in which the massive molecule of the cellulose carrier is linked to diethylamine, modelling the small active group of decarboxylase. The model reaction used in this study was that involving the elimination of carbon dioxide from bromocamphoric acids. Similar studies have also been carried out on the decarboxylase activities of various amines linked to lecithin present in solution in the form of an emulsion.[1]

The intrinsic contribution of the modelling method to enzymology at the beginning of the 1960s can be summarised as follows. It was shown that (1) a high activity and definite specificity of action can be reproduced also with the aid of materials of non-biological origin; (2) the activity of enzymes is associated with a small group of atoms which is extremely sensitive to any structural rearrangement (as a rule, these groups contain nitrogen forming part of a heterocycle or an aminoacid group, i.e. amino-nitrogen); (3) the coordination of atoms in the active group of the complex must leave a certain "reaction space"[16] which the substrate molecule can enter; (4) the "carrier" (in enzymes this is a protein) alters both the activity and the specificity of the action of the catalyst.

The question of the role of the macromolecular component in enzymes (the protein) remains, however, unanswered. What physicochemical factor or factors cause such influence by the protein component of the enzyme molecule on the reactivity of the active group? An answer to this question is of fundamental importance for the problem of creating synthetic highly active and selective catalysts. When the protein nature of the macromolecular component of the enzyme is in fact essential for the operation of the kinetic properties of enzymes, the prospects for creating enzyme-like catalysts of practical importance are extremely remote.

The report that the protein component of the enzyme papaine can be shortened almost by 90% by treatment with proteolytic enzymes without an appreciable loss of catalytic properties attracted much attention. Although this result did not throw light on the role of the protein in the enzyme, it undoubtedly "inspired" investigators concerned with the modelling of enzymes. Subsequent studies showed, however, that the specific activity characteristic of papaine is retained following a decrease of the number of aminoacid residues only from 187 (in papaine) to 75–80 (in the active enzyme).[35]

Tests of the results of studies on the fragmentation of papaine showed subsequently that this result was also erroneous.[36] In many of the other enzymes investigated it was likewise impossible to observe the retention of activity following a significant shortening of the protein chain. The question of the possible role of the protein component in enzymes as a factor determining their catalytic properties is discussed below.

IV. METAL COMPLEXES AS MODELS OF CATALASE AND NITROGENASE

The development of the thermodynamics of successive complex formation and the rapid accumulation of quantitative data concerning the stability constants of various metal complexes in the 1960s made it possible to carry out systematic investigations of a series of complexes of copper(II) ions, ranging from Cu^{2+} to the copper-containing protein haemocyanine, and iron(III) ions, ranging from Fe^{3+} to catalase. These investigations have been summarised[37] and have been partly described in another communication.[38] The level of development of the kinetic methods for the investigation of complex processes made it possible to operate not only with the concept of the effective catalytic activity but also with the characteristics of the process mechanism, including the rate constants for the individual stages in the most thoroughly investigated systems.[39-44]

It was shown in these studies that mononuclear complexes of copper and iron ions induce a radical-chain decomposition of hydrogen peroxide with participation of the metal complex in the initiation, propagation, and termination stages. Depending on the concentrations, the chain length varies from 3 to 50.

Thus, when more stringent requirements are imposed as regards the similarity of the properties of the enzyme and model in terms of the isotypical nature of the fundamental process mechanism, the mononuclear copper(II) and iron(III) complexes cannot be regarded as models of catalase.

Only the copper complexes whose oxidation-reduction potentials are appreciably positive, permitting the Cu(II) ↔ Cu(I) transitions in the rate-limiting chain initiation and propagation stages proved to be catalytically active. The incorporation of an oxygen-containing ligand into the coordination sphere or the formation of a copper(II) complex with four nitrogen-containing ligands lead to an unfavourable alteration of the oxidation-reduction potential and a loss of catalytic properties by the metal complexes. When the latter interact with the peroxide anion, there is hardly any generation of radicals.

The molecular mechanism of catalysis characteristic of catalase and many other metalloenzymes operates only in the case of Cu^{2+} complexes with triethanolamine[45] and Fe^{3+} complexes with ethylenediaminetetra-acetic acid[46] incorporating two metal ions in close proximity, which act as a cooperative acceptor-donor of an electron pair.

The study of catalase[47] led to the conclusion that the four ferriporphyrin groups present in catalase are also involved in the decomposition of H_2O_2 cooperatively and not autonomously. The molecular mechanism of the catalysis of the decomposition of H_2O_2 by haemocyanine is also determined by the presence in its structure of pairs of proximate copper ions,[48] jointly participating in two-electron oxidation-reduction transitions.

It is noteworthy that the first hypothesis concerning the joint action of a pair of iron ions in catalase was put forward in 1932,[49] while studies which demonstrated the transformation of the catalase activity into the peroxidase activity on dissociation of catalase into four subunits containing one iron ion each have played a significant role in reaching the conclusion that the active centre of catalase includes not less than two iron ions.[50]

In 1967–1968 Purmal'[51,52] formulated the hypothesis of a special role in oxidation-reduction catalysis of dinuclear and polynuclear complexes capable of acting in accordance with the mechanism of molecular catalysis. In these studies attention was also drawn for the first time to the polynuclear character of the majority of oxidation-reduction metalloenzymes.

In the above hypothesis it was assumed that in the case of a pair of metal ions in close proximity, each of which is a one-electron oxidation-reduction agent, there is a possibility of the simultaneous transfer of an electron pair between the substrate and the catalyst, which determines the molecular mechanism of catalysis. The two-electron oxidation-reduction corresponds to the transition from one stable valence-saturated state of the substrate to another. For the vast majority of substrates, such a process is therefore energetically more favourable than the transition of the substrate from a stable form into a reactive radical formed by a one-electron transfer. Thus the mechanism of molecular catalysis can compete successfully with the mechanism of radical reactions when the latter is not a chain mechanism with a fairly long chain length. In the case of metal ions which are characteristic two-electron agents such as thallium, for example, acting in accordance with a two-electron transfer mechanism in their interaction with organic or inorganic substrates, there is no necessity for the cooperation of two metal ions. An analogous behaviour obtains for the iron(III) complex of triethylenetetramine, already mentioned, the mechanism of the catalysis by this complex involving Fe(II) ↔ Fe(IV) transitions. The catalysis of the decomposition of H_2O_2 by nickel(II) complexes of monoethanolamine apparently takes place similarly, involving Ni(I) ↔ Ni(III) transitions.[53,54] For this complex, the radical component of the process is virtually absent and monoethanolamine is not oxidised. (This system was subsequently used in laboratory practice for the non-radical decomposition of hydrogen peroxide in the presence of organic compounds.) Cooperation in the form of the formation of binuclear or polynuclear complexes with metal ions in close proximity is essential for ions whose stable oxidation states differ by unity. The polynuclear nature of metalloenzymes determines the possibility of catalysis by the latter of oxidation-reduction reactions via mechanisms not involving the intermediate formation of free radicals.

Thus the study of an enzyme and model systems with various structural and electrochemical characteristics led to the idea that dinuclear and polynuclear complexes play a special role in the chemical and biochemical catalysis of oxidation-reduction reactions. This idea was subsequently confirmed and developed in further investigations.

One should note that studies of the catalase process constituted a major stage in the history of the development of research into the modelling of enzymes. Another process whose modelling is likely to have great practical value is that involving the fixation of molecular nitrogen. Here too, although at a higher level, the evolution of studies on the modelling of catalase, beginning with the investigation of very simple models, was repeated. For a long time, it seemed that the ability to fix inert molecular nitrogen under mild conditions is characteristic solely of the biochemical systems of microorganisms. The detailed mechanism of the enzymic nitrogen fixation has not been ultimately elucidated even today although it has long been known that transition metals (molybdenum and iron) play an important role in this enzyme system. Together with the hypothesis that the transition metal complex ions can incorporate the N_2 molecule in the coordination sphere, this fact has served as a basis for the search for systems activating molecular nitrogen.

The first study by Vol'pin and Shur,[55] who achieved the chemical fixation of N_2, was published in 1964. They showed that various transition metal (titanium, chromium, molybdenum, iron, etc.) compounds are capable of effectively binding nitrogen at room temperature in aprotic media in the presence of reductants (organolithium, organomagnesium, or organoaluminium compounds, aromatic radical-anions, and powerful inorganic reductants). In the subsequent hydrolysis of these intermediates, ammonia was formed.[56] Later this kind of fixation was achieved also under catalytic conditions.[57,58] Under the influence of reductants, compounds of transition metals in low-valence states [titanium(II), vanadium(II), and molybdenum(II)], which coordinate N_2, takes place. In the subsequent stages of the reduction of the coordinated N_2, reduction products are formed: metal complex derivatives of hydrazine and ammonia.[59] The metal-nitrogen complex was first synthesised in 1965 by Allen and Zenoff from a complex incorporating N_2H_4 as the ligand.[60] The formation of complexes containing N_2 on direct interaction between molecular nitrogen and metal complexes was first established by Shilov and co-workers.[61,62] The studies enumerated above have disproved the idea that chemical fixation of N_2 under mild conditions is impossible and, although the chemical difference between the enzyme nitrogenase and metal complex systems discovered by Vol'pin and Shilov is great, the foundations for the modelling of nitrogenase were laid.

Subsequent researches into the modelling of nitrogen fixation were prosecuted from two directions: Shilov and co-workers investigated simple inorganic and organometallic models;[63–65] Likhtenshtein and co-workers[66–69] studied the structure of the active centre of the enzyme and

developed certain general approaches to the search for and the synthesis of model systems on the basis of information obtained in the investigation of the real enzyme. The situation described above, where simple compounds, down to metal hydroxides, i.e. compounds just as simple as Bredig's first models of catalase, served as models of a complex protein compound, has been repeated. However, as in the modelling of catalase, the outward dissimilarity of titanium hydroxides and nitrogenase conceals a fundamental similarity. This similarity consists in the possibility of achieving the cooperative step in the multielectron reduction of N_2. Likhtenshtein and Shilov[70] analysed the energetics of consecutive transitions in a series of reactions:

$$N_2 \rightarrow N_2H \rightarrow N_2H_2 \rightarrow N_2H_3 \rightarrow N_2H_4 .$$

As a result of the high strength of the first bond to be dissociated in N_2, successive one-electron reduction of N_2 cannot proceed at an appreciable rate under the mild conditions of biological fixation. The energetic difficulties in the reduction of nitrogen are eliminated in the four-electron synchronous reduction of N_2 to a hydrazine derivative. The dissociation of the two bonds in the N_2 molecule is compensated by the formation of new bonds with the metal centres of the catalyst, i.e. the transition

$$M \ldots N \equiv N \ldots M \rightarrow M = N - N = M$$

implies a definite rearrangement of the electron density within the metal complex. An obligatory condition governing the possibility of such a process is the involvement in the latter of at least two metal ions.

The study of the structure of the active centre of nitrogenase led to the conclusion that it contains a pair of low-valence molybdenum ions in close proximity.[66,67] On the other hand, in the hydroxide, which is a polyhydroxo-complex according to the conditions of its preparation, there is a fairly large number of metal ions close to one another.

Thus both nitrogenase and the simple models discovered in these studies are polynuclear metal complexes despite all the differences between them. A system has been found which is capable of reducing nitrogen homogeneously in protic water–alcoholic media.[71] The conditions for the formation of this system, namely the vanadium(II) complex of catechol, and the manifestation of its activity show that a polyhydroxo-complex incorporating several vanadium ions functions in this instance. An interpretation of the mechanism of the action of nitrogenase taking into account the characteristics of its structure has been described.[66,67] Its essential features reduce to the following.

Since nitrogenase is coupled to a one-electron reductant system, in particular ferredoxin, the structure of the nitrogenase active centre constitutes a kind of device for "switching" the one-electron reduction mechanism to a four-electron mechanism. The mechanism of the enzyme action includes stages involving electron transport from the surface sections towards the iron-containing cluster in the bulk of the macromolecule, the storage by the iron-containing cluster of the electrons obtained from the one-electron reductant, and the four-electron attack on the nitrogen molecule in the nitrogenyl complex with participation of at least two metal atoms (molybdenum atoms in all probability).

The discovery of the possibility of nitrogen fixation by simple model compounds has stimulated studies on these lines. These researches underwent a rigorous and complex development in England. Studies by English researchers also developed in two directions, involving the investigation of metal complexes (their structure and the relation between structural features and reactivity in relation to nitrogen fixation) and the investigation of various aspects of nitrogenase, including gene engineering. Information about the character of the bonds involving molybdenum atoms in the active centre of nitrogenase was obtained by the modelling method. The similarity of the exafs spectra (the spectra of the fine structure of the edge of the X-ray absorption) of nitrogenase and molybdenum–sulphur complexes capable of binding and activating nitrogen confirmed the hypothesis of the presence of sulphur bridges between the molybdenum atoms in the active centre of the enzyme.[72]

The chemical investigations were directed towards the study of the reactivity of the coordinated nitrogen. The formation of complexes of N_2 with various Mn, Fe, Co, Ni, Mo, and W complexes was established. The attempt to protonate the coordinated N_2 led to the decomposition of the complexes with evolution of N_2. The subsequent reaction of the coordinated N_2 with formation of $M{=}N{-}NH_2$ was observed only for the Mo and W complexes with phosphorus-containing ligands.[73,74] The formation of two moles of NH_3 was observed on subsequent protonation.[74] It was not possible to determine the intermediates in the transition from the hydrazo-complex to NH_3,[75] i.e. an independent confirmation of the multielectron mechanism of the reduction process was obtained. These results stimulated interest in the study of the mechanism of the electrochemical reduction of nitrogen complexes with metal ions bound in one way or another to the electrode surface.[76]

Exceptionally interesting results have been obtained recently in this field. The molybdenum complexes of phospholipids, adsorbed on a mercury amalgam, proved such effective reductants for nitrogen that it was possible to follow the process at room temperature and atmospheric nitrogen pressure.[77] The above principal characteristics of the mechanism of the action of nitrogenase were reflected in this model system.

The set of studies on nitrogenase and model systems led to the formulation of ideas and principles of a general character important for the theory of selection and construction of models of polynuclear metalloenzymes with an oxidation-reduction activity. The concept of multielectron transitions involving considerable changes in the nuclear configurations was put forward.[78] Likhtenshtein suggested the principle of the "optimum movement".[79] Its essential feature is that a synchronous process, accompanied by appreciable nuclear rearrangements, is favoured by the energy factor, but, when the elementary step involves many nuclei, the rate of reaction may become vanishingly small even for significantly exothermic reactions. In other words, the number of atoms involved in the reaction should be sufficiently large to ensure favourable energy relations but sufficiently small to retain a high probability of the synchronisation of the movement of nuclei along the reaction coordinate.

Theoretical procedures for the estimation of the probability of synchronisation in processes involving many nuclei have been developed.[80]

V. MODELS OF OXIDASES, OXYGENASES, AND OTHER ENZYMES

An important set of enzymes involved in terminal oxidation processes includes oxygenases and oxidases which catalyse the reactions of molecular oxygen with various organic substrates. In 1954 Udenfriend et al.[81] proposed a hydroxylating system which leads to the same hydroxylation products as certain mono-oxygenases. Udenfriend's model system includes iron ions, ethylenediaminetetra-acetate as the ligand, and ascorbic acid or its analogues as the electron donor. The identification of the chemically reactive species leading to the reaction products in this multicomponent system was for a long time difficult. The development of kinetic research methods made it possible to demonstrate that these

species in Udenfriend's system are metal–oxygen complexes having specific reactivities.[82]

Thus, in relation to this system, it has been possible to identify the intrinsic elementary step in the catalytic action in the activation of oxygen, which can be regarded as a new stage in the modelling of enzymes—the determination of the elementary mechanism of the chemical steps in the active centre of the enzyme and their reproduction in simpler systems.

The extent to which the elementary oxidation-reduction reactions of the metal complex ions are of a general character can be seen from a comparison of the catalytic functions of copper ions in various ligand environments in the oxidation of ascorbic acid by atmospheric oxygen. It has been established[83,84] that the reactive intermediate species is the oxygen complex CuO_2^+, which interacts with the substrate via a two-electron mechanism; an analogous result has been obtained also for the oxidation of methanol.[85] This elementary step models the action of a series of so-called colourless oxidases containing a copper(I) ion in the active centre. Under certain conditions, the cooperation of two copper ions is observed in the elementary step involving the two-electron oxidation of the ascorbate anion[86] or in the elementary step involving the two-electron reduction of oxygen.[87] These reactions model the non-radical cooperative processes occurring in the case of enzymes (the so-called blue oxidases) containing in the active centre two and more copper ions in close proximity.

The results of kinetic studies on relatively simple catalytic systems for the oxidation of ascorbic acid by oxygen[88] showed that the elementary step in the model and enzyme systems is in essence of the same type.

A specific feature of the enzyme system consists apparently in a three-dimensional structure of the immediate environment of the metal ion which limits the possibility of side reactions.

A number of investigations have been devoted to models of peroxidase. We shall not consider them because only a detailed kinetic study will make it possible to distinguish the "peroxidase-like" mechanism of the formation of a complex with H_2O_2 and its subsequent reaction with the substrate from the mechanism involving $H\dot{O}_2$ and $\dot{O}H$ radicals, which is characteristic of the majority of metal complexes.

A large series of comparative studies of the spectroscopic, thermodynamic, electrochemical and catalytic properties of various metal complexes and metalloenzymes, incorporating the same metal, have been carried out by Williams,[89,91] who arrived at conclusions significant for the search for syntheses of active models and also for the understanding of the specific properties of metalloenzymes. Thus, it has been shown that zinc complexes with tetrahedral but not octahedral coordination environments exhibit a carbonic anhydrase activity. The study of model systems made it possible to propose a structure for the active centre of carbonic anhydrase, where the zinc ion is present as a complex with a deformed tetrahedral structure in which two ligands consist of the sulph-hydryl groups of the protein. Comparison of the spectroscopic and thermodynamic properties of the zinc complexes of phenanthroline and the complex formed as a result of the addition of phenanthroline to the zinc atom of the active centre of alcohol dehydrogenase made it possible to demonstrate the presence of two or three vacant sites in the coordination sphere of zinc, available for substitution by the substrate. Williams[89] was the first to put forward the hypothesis, which was subsequently confirmed, that the specificity of the reactions of any metalloenzymes with small molecules (O_2, CO_2, H_2O, H_2O_2, and N_2) is determined almost completely by the substituted coordination sphere of the complex-forming metal.

In his analysis of the spectroscopic and magnetic properties of the metal complexes and metal-containing oxygen transferring agents haemocyanine and haemerythrin, Williams[91] proposed a general mechanism of their action:

$$Cu(\bar{I}) \ldots Cu(\bar{I}) + O_2 \rightarrow Cu(II)O_2^{2-}Cu(II),$$
$$Fe(II) \ldots Fe(II) + O_2 \rightarrow Fe(III)O_2^{2-}Fe(III).$$

He emphasised a characteristic feature of the functioning of these oxygen-transferring agents which is difficult to achieve in model systems: in the absence of oxygen the reduced metal ions are located in the protein structure sufficiently far from one another not to influence their magnetic and optical properties and their reactivities. Oxygen is bound as a result of the mutual approach of a pair of metal ions, which is accompanied by a change in conformation and "strain" in the protein component of the transferring agent. He put forward similar ideas concerning the nitrogen fixation mechanism. He explained the presence of molybdenum in all the nitrogen fixing system by the fact that the following process can be formulated only for two molybdenum(III) ions:

$$Mo(III)N_2Mo(III) \rightarrow Mo(VI)(N^{3-})_2Mo(VI) \rightarrow 2NH_3.$$

The difficulty of modelling this system arises from the fact that two molybdenum(III) atoms which have approached one another must not form a strong Mo–Mo bond, retaining at the same time a vacant site in the coordination sphere for the formation of the complex with N_2.

One should note briefly that, simultaneously with the development of studies on the modelling of metalloenzymes, research into organic catalysts modelling the action of particular metal-free enzymes has developed fairly vigorously. Extensive information about these problems has been published.[92,93]

VI. THE MODELLING OF ENZYMES AS A PATHWAY TO NEW CATALYSTS

The development in the USSR of the second of the trends specified above (the synthesis of catalysts on the basis of the existing information about the structure and properties of enzymes and the principles of enzyme catalysis) was initiated successfully and logically in the USSR at the beginning of the 1960s by Khidekel'.[94–102] There is no doubt about the initial general postulate—that of the characteristics of the action of coenzymes and enzymes can be explained in principle on the basis of the fundamental postulates of organic, coordination, and polymer chemistry. However, the "unmapped regions" as regards information about systems of biological origin can pose stringent requirements on the intuition of investigators who choose this pathway.

The simplest systems, namely the complexes of copper ions with various amines, were investigated as analogues of copper-containing phenol oxidases in the initial stage of these studies.[94,95] With the aid of such catalysts, it was possible to vary widely the direction of the reactions as a result of the formation of complexes of the intermediate compounds or starting materials with the catalyst and by the variation of the composition of the catalysts. These results proved to be useful in carrying out oxidation reactions involving various phenols. It was possible to develop convenient methods for the synthesis of a number of quinonoid compounds, naphthols, and spirocyclic trimers.[96,97]

The retrospective analysis of the evolutionary pattern of the biogenesis of enzymes has been important for the selection of procedures for the synthesis of their analogues with different degrees of complexity in structure and organisation.[98,99]

Studies have been made on a series of dihydropyridine derivatives—analogues of the coenzymes nicotinamide-adenine dinucleotide and nicotinamide-adenine dinucleotide phosphate. New highly active reduction systems and catalysts for the hydrogenation of olefins, significantly superior to the existing liquid-phase hydrogenation catalysts, were obtained on the basis of these investigations.

It was possible to create new types of homogeneous and "heterogenised" complex hydrogenation catalysts—analogues of the enzyme hydrogenase. Catalysts based on the following systems were obtained: 1,4-dihydronicotinamide—a transition metal derivative, low-valence transition metal complexes with quinones and aromatic compounds, aromatic carboxylic acids, aminoacids and peptides, dyes of various types, hydroxyquinones, and aromatic hydroxyazo-compounds. Some of these catalysts proved to be suitable for a series of processes involved in fine and fundamental organic synthesis.[100] A series of studies have been devoted to the transfer of activated hydrogen by methods which are tentatively similar to the enzyme procedures.[101] Using these methods, it was possible to hydrogenate at a high rate ketones, aldehydes, and aromatic compounds and to achieve a series of selective hydrogenation processes (in particular, the reduction of the carbonyl group in the presence of the C=C double bond[102]). Systems incorporating a catalyst activating molecular hydrogen and a catalyst for the transfer of activated hydrogen have also been created.[101]

Catalytic systems of the above type make it possible to reduce at a high rate and with a high specificity a large number of organic and complex compounds.

The results concerning the catalytic hydrogenation of aromatic compounds and aromatic nitro-compounds were particularly valuable. Some of the new catalytic systems developed have been incorporated in industrial practice.[103-106]

Extensive information about systems in which homogeneous hydrogenation is effected by complexes of metals of all the Groups in the Periodic System has been published.[107] The catalysts described include those in the creation of which various natural hydrogenases served as the mobilising system.

A new interesting type of modelling of various enzymes was initiated following the development of the synthetic chemistry of polymers containing various functional groups (carboxy-, amino-, etc. groups), which are soluble in polar solvents.

The investigation of the catalytic properties of such polymers and their complexes with metal ions in the USSR was developed in the studies of Kabanov, Pshezhetskii, and Kirsh.[108-113] The activity of systems based on polyacrylic acids, polyethyleneimine, polyvinylpyridine, etc. relative to the catalase, peroxidase, ascorbic acid oxidase, catechol 1,2-oxygenase, and proteolytic functions exceeded by a factor of 10^3–10^4 the activity of the low-molecular-weight analogues, being inferior by a factor of 10^2–10^3 relative to the activities of the enzymes modelled.

VII. THE ROLE OF THE MACROMOLECULAR COMPONENT IN MODEL SYSTEMS AND OF THE PROTEIN IN ENZYMES

The study of the simplest model system has shown that their catalytic properties are "improved" when the low-molecular-weight active group is combined with a high-molecular-weight group. The stability of systems of the type of "active group–carrier" rises, while their catalytic activity as a rule also increases.

The modelling of enzymes by an independent procedure led to the conclusion that their high catalytic activity is associated with the protein, macromolecular nature of these systems. To a lesser extent, the study of model systems revealed the role of the protein as a factor determining the selectivity of the enzyme action. Nevertheless, this function of the protein component of the enzyme molecule was established initially on a speculative basis in terms of the "key–lock" model, and then also experimentally. Koshland's principle of induced correspondence gained wide recognition.[114-115] It became understood why the selectivity of enzyme action was associated with a high degree of steric correspondence between the substrate and the active centre in the enzyme structure. The factor determining this correspondence is the high structured organisation of the enzyme—up to a quaternary organisation. The absence of such organisation from model systems is sufficient to understand why the creation of a simple model with a high specificity of action in relation to polyatomic substrates is a problem unlikely to have a successful solution.

The choice of activity as the principal property of models constituted a psychologically understandable stimulus for calculations by investigators, who tried to show that the activity of their models is comparable or even superior to that of enzymes. In such calculations the activity is referred, for example, to the unit weight of the catalyst; the pH-dependent activity of the model is extrapolated to the pH range in which the enzyme functions, etc. On the other hand, when calculated data are disregarded, one may conclude that it has not been possible to create a model equal to the enzyme in its activity for their equal molar concentrations at similar pH, temperature, and substrate concentration.

The idea of the possible role of the protein as a factor determining the high activity of enzymes was put forward for the first time by Bauer in 1935,[116] who suggested that the protein can exist in equilibrium and non-equilibrium states; during the enzymic reaction, the protein passes from a non-equilibrium to an equilibrium state, while the energy of the transition is used to overcome the activation barrier to the reaction of the substrate. The energy evolved as a result of the enzymic reaction returns the protein molecule to the initial non-equilibrium state. The general principle of the possibility of employing the energy of a chemical reaction to accelerate the reaction under consideration, which appeared during the period when Semenov created the theory of branched chain reactions, was reflected in Bauer's hypothesis.

Kobozev examined from the same standpoint the problem of the relation between the catalytic activity of a low-molecular-weight compound and the properties of the high-molecular-weight substance attached to it.[117,118] His idea consisted in the hypothesis that the thermodynamically non-equilibrium mass should increase the catalytic activity of the species linked to it with respect to various reactions. He showed that in many instances a logarithmic relation is observed between the activity and the magnitude of the attached non-equilibrium mass. The specific question of the increase of catalytic activity of a species as a result of the addition of a protein to it has also been examined.[119,120] The role of the protein macromolecule is to participate in the recovery of the energy: the energy evolved in the course of the reaction is not scattered in the form of heat but is used to activate the catalytic centre.

A number of studies have been made whose aim was to specify in greater detail the problem of the possible forms of the accumulation of energy by the protein molecule.[121,122] Various approaches to the elucidation of the role of the protein in enzymes has been analysed by Blyumenfel'd.[123] His review can be supplemented only by the hypothesis of the entactic (extended, strained) state of the active centre of the enzyme put forward on the basis of the analysis of a series of model and enzyme systems.[91] According to this

hypothesis, the small activation barrier to the enzymic reaction is determined by the fact that, even before the enzyme combined with the substrate, the active centre of the enzyme contained a functional group with a high potential energy. The increased energy in the region of the active centre arises by virtue of the conformational energy of the entire protein molecule. Thus the zinc atom in carboxypeptidase or carbonic anhydrase is much more reactive than in its initial ionic form or in a complex with free low-molecular-weight ligands. When it is located in the active centre, the zinc atom is only partly bound to the protein ligands forming the strained configuration of a distorted tetrahedron. The possibility of such formations is a specific feature of the macromolecular polyligand (the protein), characterised by the presence of secondary and tertiary structures.

According to Blyumenfel'd, the conformational transformations of the protein are indissolubly linked to the elementary step in the enzymic reaction: the latter consists in a conformational change in the macromolecule (of the enzyme–substrate complex) and the rate of the substrate–product transformation is determined by the rate of this conformational change[123] (p.155). In contrast to the views presented above, in Blyumenfel'd's concept the protein molecule incorporating the active centre is in a conformationally equilibrium state before the start of the interaction with the substrate. In the region of the active centre the protein molecule passes to a conformationally non-equilibrium state only for the enzyme–substrate compound. The transition from the conformationally non-equilibrium state to the equilibrium state involves greater or smaller changes in the structural organisation of the protein—the dynamics of conformational changes. One of the most thoroughly developed dynamic models is that describing the functioning of the enzyme aspartate aminotransferase.[124]

Without considering in greater depth the current problems of modern theoretical enzymology, one can apparently speak of a relation between the high catalytic activity of enzymes and the structural-dynamic characteristics of the protein. Thus not only the selectivity of their action but also the catalytic activity of enzymes is associated with the fact that the protein consists of macromolecules with a structural organisation, the changes in the latter making the same contribution to the enzymic step as the redistribution of chemical bonds in the substrate species.

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The question arises of the prospects for the creation of model catalysts with activities and selectivities similar to those of enzyme catalysts. The solution of this problem, which involves in essence the creation of synthetic analogues of enzymes rather than models, is associated with the creation and employment of polymers having a flexible structural organisation, like proteins. Naturally, this is not the only possible way of achieving a solution. It may be that the procedure involving the combination of polymers of the above kind, linked to active groups, with systems of molecular sieves of the type of zeolites will lead to success. It is also possible that an unpredictable solution will be found. This does not imply that the study of low-molecular-weight models of enzymes has lost its value. Their investigation will lead to the formulation of new hypotheses and concepts useful for the solution of practical problems.

However, one should not overestimate the role of studies on the modelling of enzymes as a method for the investigation of the latter. In this sense the modelling method is simply one of the trends in the overall research programme, including the study of the sequence of aminoacid residues in enzymes, the X-ray diffraction analysis of proteins, the determination of the nature of coenzymes, the study of the kinetics and mechanism of enzymic reactions, the identification of intermediate compounds, the investigation of the conformational states of the enzyme protein and the dynamics of the changes in these states, etc.

This field of research has already yielded promising practical results associated with the synthesis of highly active non-protein catalysts.

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Thiadecalins and Condensed Thiacyclohexanes of the 2-Thiabicyclo[4.3.0]nonane Series

S.K.Klimenko and T.V.Stolbova

The latest advances in the chemistry of condensed bicyclic thiacyclohexanes of the type of thiadecalins and their analogues are examined. The results of studies on the methods of synthesis, chemical reactions, and the conformational and configurational analysis of thiadecalins, their analogues, and derivatives are surveyed.
The bibliography includes 99 references.

CONTENTS

I. Introduction 476
II. Methods of synthesis 476
III. Structure and properties 481

I. INTRODUCTION

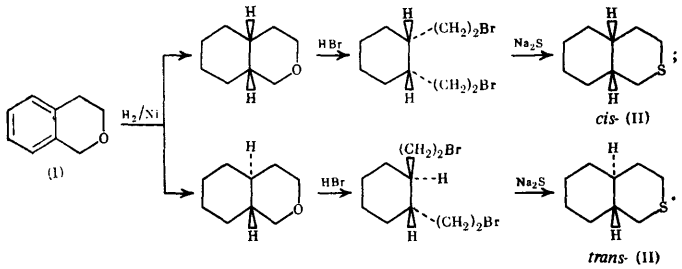
Particularly vigorous development of thiacyclohexane chemistry has occurred in the last two decades, as shown by the list of literature references quoted in this review. Major advances have been achieved in the development of synthetic methods in the synthesis of derivatives (sulphoxides, sulphones, sulphamides, sulphonium salts, and oxosulphonium salts), and in the study of the reactions and stereochemical characteristics of the structures of both the sulphides themselves and their derivatives. Whereas the original development of this field was in many respects due to the problem of the identification and utilisation of petroleum sulphides,[1,2] the shift of recent studies towards stereochemistry indicates the undoubted theoretical interest of the condensed thiacyclohexanes, primarily as thioanalogues of decalin. At the same time the search among them for substances with properties of practical value holds out much promise. It is known that certain derivatives of sulphoxides have been recommended as surfactants, flotation agents, oxidation and corrosion inhibitors, insecticides, solvents, and rare metal extractants.[3-11] The S-methylsulphonium salts play an important role in processes occurring in the living organism.[12] Among sulphonium salts, biologically active compounds[13] are being sought and thioanalogues of steroids are being synthesised.[14]

II. METHODS OF SYNTHESIS

1. *cis*- and *trans*-2-Thiadecalins derived from 1-(2-Bromoethyl)-2-Bromomethylcyclohexane

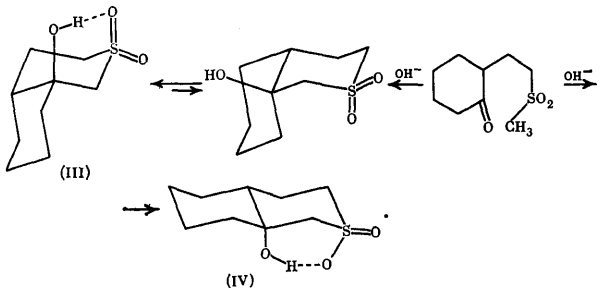
The synthesis of even the simplest condensed thiacyclohexanes is complicated by the fact that each of them can exist in two stereoisomeric forms. The synthesis of *cis*- and *trans*-2-thiadecalins (II) from isothiochroman (I) involves the preparation of 3-oxocyclo[4.4.0]decanes, the resolution of the stereoisomers, their conversion into the dibromides, and their subsequent cyclisation with sodium sulphide[15] (see the formula below).

Together with 1-thiadecalin, 2-thiadecalins (II) have been isolated from petroleum by extraction with an aqueous solution of mercury acetate.[1]

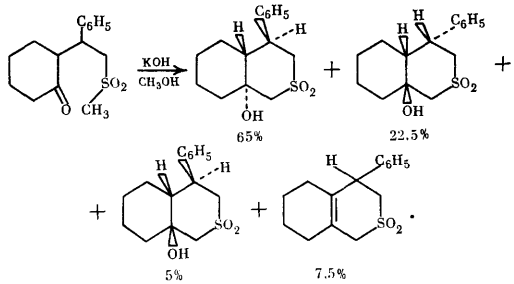


2. The Sulphones of *cis*- and *trans*-9-Hydroxy-2-Thiadecalins derived from 2-(2-Methanesulphonylethyl)cyclohexanone

The intramolecular cyclisation of 2-(2-methanesulphonylethyl)cyclohexanone under the conditions of base catalysis proceeds via the α-sulphonylcarbanion and leads to *cis*-9-hydroxy-2-thiadecalin 2,2-dioxide (III) and its *trans*-isomer (IV).[16] In the *cis*-isomer the conformation with the axial hydroxy-group is fixed by the intramolecular hydrogen bond:[16]



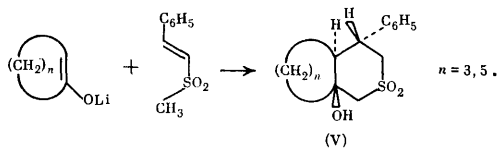
The cyclisation of 2-(α-methanesulphonylmethyl)benzylcyclohexanone under analogous conditions takes place with formation of 9α-hydroxy-4β-phenyl-*trans*-9β-hydroxy-4α-phenyl-*cis*-, and 9β-hydroxy-4β-phenyl-*cis*--2-thiadecalins 2,2-dioxides† and of the hydration product:[17]



The initial ketosulphones are obtained from 1-pyrrolidino or 1-morpholino-cyclohexene and αβ-unsaturated sulphones.[18] The cyclisation products have been separated by preparative chromatography and the configurational assignments have been made on the basis of ^{1}H NMR and infrared spectra; the *cis*-elimination reactions have also been achieved for the *O*-acetyl derivatives.[16,17]

3. Cyclisation of the Lithium Enolates of Cycloalkanes and Methyl Styryl Sulphone

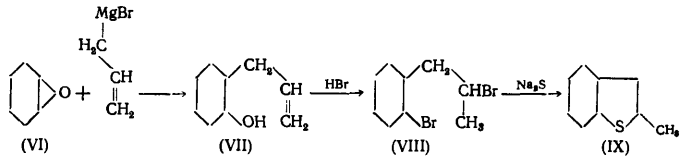
Derivatives of sulphones of 2-thiadecalin and its analogues, differing in the size of the condensed alicyclic 3-thiabicyclo-[4.3.0]nonane and 3-thiabicyclo[4.5.0]undecane# can be obtained by cyclising methyl styryl sulphone with the lithium enolates of cycloalkanes on heating in the 1:2 tetrahydrofuran (THF)–dimethylformamide (DMF) mixture. The yields of the final products (V) are 76–100%. The structural assignments have been made by means of ^{1}H NMR:[19]



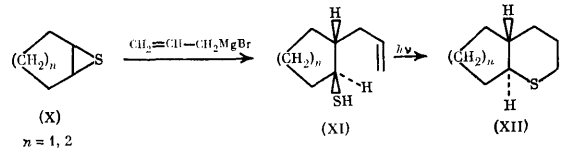
(V)

4. *trans*-1-Thiadecalins and *trans*-2-Thiabicyclo[4.3.0]-nonanes derived from Cycloalkene Sulphides and Allylmagnesium Bromides

Up to 1970 it was not possible to synthesise *trans*-1-thiadecalin. It seemed that the same method could be used for its synthesis as that for the synthesis of 2-thiadecalins but the synthesis of the corresponding dibromo-derivatives presents certain difficulties. Thus the interaction of epoxycyclohexane (VI) with allylmagnesium bromide and the subsequent reaction of 2-allylcyclohexanol (VII) with hydrogen bromide lead solely to 1-bromo-2-(2-bromopropyl)cyclohexane (VIII) whose cyclisation with sodium sulphide gives rise to a mixture of stereoisomers of 2-methyl-1-thiahydrindan (IX):[20]

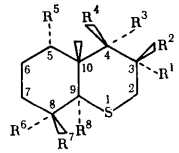


However, later the same workers[21–23] proposed the synthesis of *trans*-1-thiadecalins (XII) by the interaction of cyclo-olefin sulphides (X) with allylmagnesium bromide and subsequent intramolecular cyclisation of the allylcycloalkanethiols (XI) formed in this process:



1-Thiahydrindans or 2-thiabicyclo[3.3.0]octanes arise in the given reaction as side products.[21–23] The cyclisation of 2-allylcyclohexanethiol (XI, $n = 2$) with formation of a mixture of 1-thiadecalin (XII) and 2-methyl-1-thiahydrindan in proportions of 2:1 has been observed even after its prolonged storage; after ultraviolet irradiation, 1-thiadecalin is formed in a large amount, while on treatment with 75% sulphuric acid the product is 2-methyl-1-thiahydrindan. When crotylmagnesium bromide is used, a mixture consisting of two pairs of isomers, namely those of 4-methyl- 1-thiadecalin and 2,3-dimethyl-1-thiahydrindan, is formed in the same reaction.[22]

Despite the difficulties indicated, associated with the formation of side products, it has been possible to obtain 1-thiadecalin,[21] 4-methyl-1-thiadecalin,[22] 9-methyl-1-thiadecalin,[23] and 2-thiabicyclo[4.3.0]nonane.[24] Although the configurations of the intermediate and final products have not been investigated, the above sulphides have been described as the *trans*-isomers on the assumption that reactions involving the ring opening in the *cis*-sulphides are stereospecific and are accompanied by the formation of mercaptans with the *trans*-configuration, while no change in configuration takes place in the heterocyclisation reaction.[23] This hypothesis proved to be correct. The method proposed[21–23] has been used in another study[25] for the synthesis of 3-, 4-, 5-, 8-, and 9-monomethyl-substituted *trans*-1-thiadecalins (XII)–(XX); their configurations as well as the configurations of the initial sulphides and intermediate *trans*-2-allylcyclohexanethiols have been established by ^{13}C NMR.



(XII) all R = H; (XIII)*R^1 = 3α-CH_3; (XIV) R^3 = 3β-CH_3; (XV) R^3 = 4α-CH_3; (XVI) R^4 = 4β-CH_3; (XVII) R^5 = 5α-CH_3; (XVIII) R^6 = 8α-CH_3; (XIX) R^7 = 8β-CH_3; (XX) R^8 = 9-CH_3.

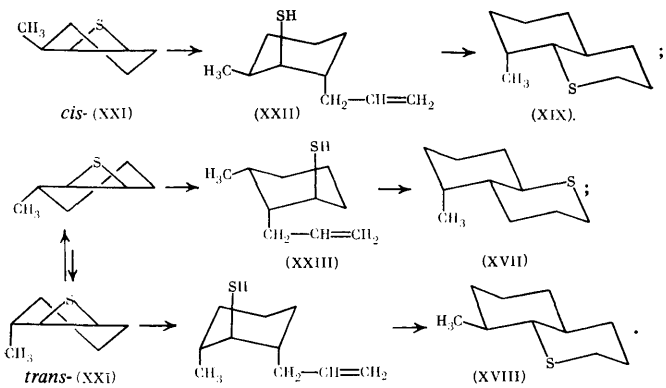
†The symbol β denotes substituents located on the same side of the ring as the hydrogen atom at C(10), while the symbol α denotes substituents on the opposite side of the ring in relation to this hydrogen atom.

#Since there is no uniformity in the literature quoted below in the names used for the same compounds, we adopted as a basis the term "thiadecalins" and, in the absence of trivial names, the term "thiabicycloalkanes".

*The substituents R not indicated here and henceforth are H atoms.

It has been shown[25] that the use of azobisisobutyronitrile (0.1 M) as the initiator of the intramolecular radical cyclisation of *trans*-2-allylcyclohexanethiols reduces to a minimum the formation of 1-thiahydrindans and thus leads to better results compared with initiation by ultraviolet irradiation.[21-24]

We shall now consider the stereochemistry of the reaction of 3-methylcyclohexene sulphide (XXI) with allylmagnesium bromide.[25] The reaction of the *cis*-isomer of compound (XXI) is accompanied by the opening of the three-membered ring with formation of compound (XXII) as an intermediate [with the *trans*-configurations at C(1) and C(2)], whose subsequent cyclisation yields only 8β-methyl-*trans*-1-thiadecalin (XIX) (in 90% yield).



cis-(XXI) (XXII) (XIX);

(XXIII) (XVII);

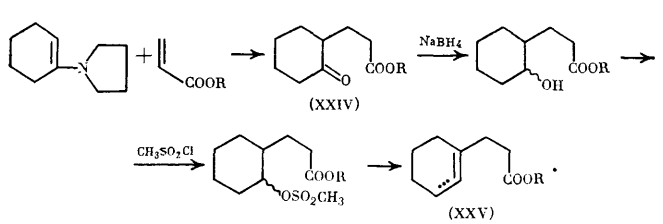
trans-(XXI) (XVIII).

If a mixture of the *cis*- and *trans*-isomers of compound (XXI) (38 and 62% respectively) is used in the reaction, then the same thiadecalin (XIX) (63%) is obtained as the main product after cyclisation despite the fact that *trans*-(XXI) predominated in the initial mixture. By virtue of its greater stability, *trans*-(XXI) reacts with allylmagnesium bromide only partially and only two products, (XVII) and (XVIII), are formed from it in comparable amounts (11 and 13%). The attack on the preferred conformer of *trans*-(XXI), leading to compound (XVII), is probably difficult for steric reasons.[25]

The *trans*-1-thiadecalins (XIII) and (XIV), arising in the cyclisation of the corresponding mercaptans, have been detected in proportions of 1:30, which can be accounted for by the addition of the thiol to the double bond in the *trans*-position in the usual manner.[25]

5. The *cis*- and *trans*-1-Thiadecalins derived from 3-(2-Oxocyclohexyl)propionates

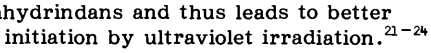
Method (a). It is known[26] that the condensation of pyrrolidinocyclohexenes with acrylates leads to 3-(2-oxocyclohexyl)propionates (XXIV), which can be converted into the isomeric 3-cyclohex-1-enyl or 3-cyclohex-2-enyl propionates (XXV):[25,27,28]



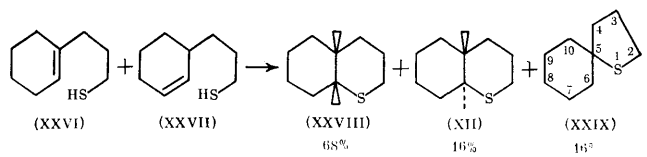
(XXIV)

(XXV)

The latter are converted into 1- and 3-(3-mercaptopropyl)-cyclohexenes in accordance with the scheme[14,25]

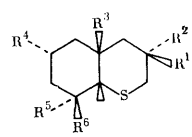


The radical heterocyclisation of (3-mercaptopropyl)cyclohexenes (XXVI) and (XXVII) takes place preferentially with formation of *cis*-1-thiadecalins.[21] Thus, on heating with azobisisobutyronitrile in benzene, compounds (XXVI) and (XXVII) give rise to mixtures of *cis*-1-thiadecalin (XXVIII) (68%), *trans*-1-thiadecalin (XII) (16%), and 1-thia-spiro[4.5]-decane (XXIX) (16%). The predominance of the *cis*-1-thiadecalin (XXVIII) in the mixture is associated with the fact that the thioradicals add to cyclohexenes preferentially with formation of axially substituted thiacyclohexanes:[14,25,26,29]



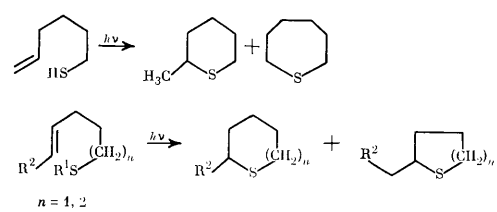
(XXVI) (XXVII) (XXVIII) 68% (XII) 16% (XXIX) 16%.

The mixtures of the products (XII), (XXVIII), and (XXIX) were separated by precipitation and recrystallisation of the complexes with $HgCl_2$ and by preparative gas–liquid chromatography (GLC). The configurations of the products were determined with the aid of ^1H and ^{13}C NMR. The 3-, 6-, 8-, and 10-monomethyl-*cis*-1-thiadecalins (XXX)–(XXXV) were isolated and characterised in this way.[25]



(XXVIII) all R = H; (XXX) $R^1 = 3\beta\text{-}CH_3$; (XXXI) $R^2 = 3\alpha\text{-}CH_3$; (XXXII) $R^3 = 10\text{-}CH_3$; (XXXIII) $R^4 = 6\alpha\text{-}CH_3$; (XXXIV) $R^5 = 8\alpha\text{-}CH_3$; (XXXV) $R^6 = 8\beta\text{-}CH_3$.

The formation of condensed thiepans can be expected in this reaction on the grounds that the photochemical cyclisation of unsaturated acyclic mercaptans or sulphides yields five-, six-, and seven-membered thiacycloalkanes:[30,31]

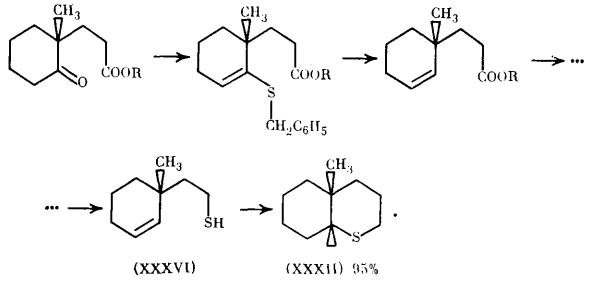


$n = 1, 2$

However, condensed thiepans were not isolated in the above reaction, which can be accounted for by the high steric requirements of the latter.[25]

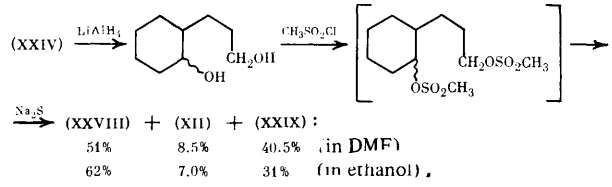
Method (b). A method described previously for 4-thia-5β-cholestanes has been used successfully in the synthesis of 10-methyl-*cis*-1-thiadecalin (XXXII).[14] 3-(1-Methyl-2-oxocyclohexyl)propionate is converted into the *S*-benzyl derivative of the thioenol by heating with benzylmercaptan in benzene. Subsequent desulphurisation of the *S*-benzyl derivative of the thioenol on activated Raney nickel leads to 3-(1-methyl-2-cyclohexenyl)propionate, which, as shown above, is subsequently converted in four stages into the

mercaptan (XXXVI) and is cyclised in the presence of azobisisobutyronitrile into 10-methyl-*cis*-1-thiadecalin (XXXII):[25]



(XXXVI) (XXXII) 95%

Method (c). The reduction of 3-(2-oxocyclohexyl)propionate (XXIV) with lithium aluminium hydride affords a mixture of the *cis*- and *trans*-diols which are treated with methanesulphonyl chloride and are converted, without isolating the bismethanesulphonates, into the *cis*- and *trans*-1-thiadecalins (XXVIII) and (XII) by heating with sodium sulphide in DMF or 50% methanol.[25] This makes it possible to reduce the number of intermediate stages:



(XXIV) → (XXVIII) + (XII) + (XXIX):

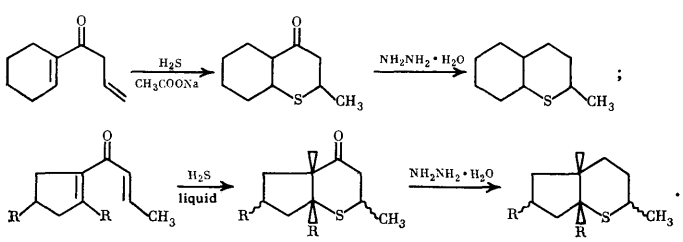
51%	8.5%	40.5%	(in DMF)
62%	7.0%	31%	(in ethanol).

1-Thiaspiro[4.5]decane (XXIX) is formed as a side product in a considerable amount. The methyl-substituted 3-(2-oxocyclohexyl)propionates behave analogously.[25]

The preferential formation of *cis*-1-thiadecalins and spirans of the type of compounds (XXVIII) and (XXIX) in the reaction considered is caused by the ready elimination of the axial methanesulphonyl group with subsequent addition of the mercapto-group to the double bond formed. The overall result of the reaction is very close to that obtained in the cyclisation of 3-(3-mercaptopropyl)cyclohexenes [see methods (a) and (b)].

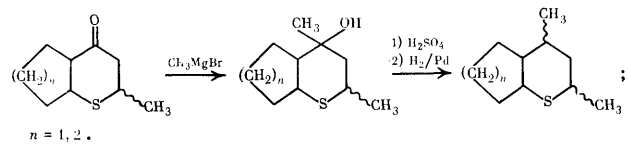
6. 2-Methyl-1-Thiadecalins derived from 2-Methyl-1-Thia-4-Decalones

The initial 2-methyl-1-thia-4-decalones can be synthesised by the familiar reaction of ketodienes with hydrogen sulphide.[32–34] A mixture of the isomers of 2-methyl-1-thia-4-decalone is formed from 1-(3-butenoyl)cyclohexene and hydrogen sulphide in the presence of sodium acetate.[35,36] The keto-group in the thiadecalones can be reduced by hydrazine hydrate with formation of 2-methyl-1-thiadecalins as a mixture of stereoisomers, which is a significant disadvantage of the method as a whole.[37–39] A mixture of the four isomeric 2-methylthiadecalins were separated chromatographically.[39]



2-Thiabicyclo[4.3.0]nonanes are obtained in accordance with an analogous scheme from the corresponding cyclopentene derivatives.[37,38] The cyclisation of ketodienes containing the planar cyclopentane ring proceeds with more difficulty and the introduction of the methyl group into the five-membered ring gives rise to additional steric hindrance. The reaction can be achieved after a considerable increase of the hydrogen sulphide concentration, which is attained by employing liquid hydrogen sulphide. The formation of derivatives of the *trans*-series in the form of five-membered derivatives is virtually ruled out.[37]

The interaction of the above ketosulphides with Grignard reagents makes it possible to synthesise 2,4-dialkyl-2-thiabicycloalkenes:[40]

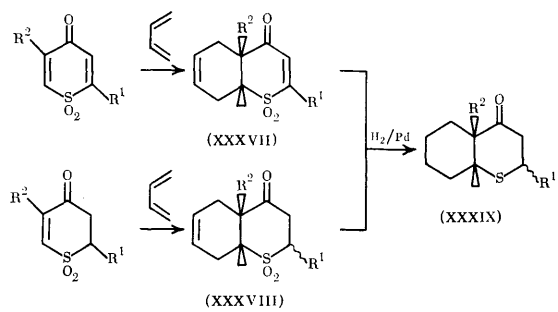


$n = 1, 2$.

Mixtures of 2-thiabicycloalkenes containing the double bond in the α-, β-, and γ-positions relative to the heteroatom are formed from cyclic carbinols on dehydration with sulphuric acid. It has been noted that the hydrogenation of these 2-thiabicycloalkenes in the presence of 5% Pd/C at 50 °C and a hydrogen pressure of 50–70 atm proceeds with difficulty and does not go to completion.[40,41]

7. The Diels–Alder Condensation of Thiopyrone and Dihydrothiopyrone Sulphones with Dienes

The Diels–Alder reaction of 4-thiopyrone and 2,3-dihydro-4-thiopyrone 1,1-dioxides with butadiene constitutes a convenient method of synthesis of the thermodynamically less stable *cis*-isomers. The condensation of 4-thiopyrone 1,1-dioxide with butadiene proceeds slowly even at room temperature, while on heating in an autoclave at 100 °C in dioxan it gives rise to 5,8,9,10-tetrahydrothiochroman-4-one 1,1-dioxide in 40% yield.[42] This method was later employed in other investigations.[36,43] Thus the corresponding oxosulphones (XXXVII) have been obtained from 2-methyl- and 2,5-dimethyl-4-thiopyrone 1,1-dioxides and butadiene. 2,5-Dimethyldihydrothiopyran-4-one 1,1-dioxide gives rise to a mixture of the stereoisomeric products (XXXVIII) differing in the position of the CH_3 group at C(2).[36] 2,3-Dihydrothiopyran-4-one 1,1-dioxide reacts with butadiene in benzene to form the condensation product in quantitative yield:[43]

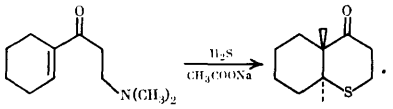


(XXXVII) (XXXVIII) (XXXIX)

The bicyclic sulphones obtained give rise to mixtures of stereoisomers (XXXIX) on reduction in the presence of palladium in dioxan or platinum in an acid medium, incomplete reduction of the keto-group to the hydroxy-group being observed in the latter case.[36] In the presence of acids, the *cis*-isomers of the oxosulphones ($R^2 = H$) isomerise to the corresponding *trans*-isomers as a result of inversion at the C(10) atom in the enolisation process.[43]

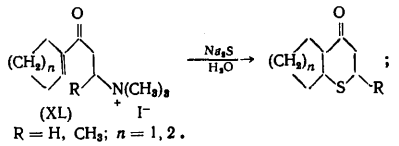
8. Thia-4-Decalones and 2-Thiabicyclo[4.3.0]-5-Nonanones Derived from 1-(3-Dimethylaminopropanoyl)cycloalkenes and Their Methiodides

On reaction with hydrogen sulphide in the presence of sodium acetate and subsequent heat treatment, 1-(3-dimethylaminopropanoyl)cyclohexene cyclises to form *trans*-1-thia-4-decalone (in 50% yield):[44]



1-(3-Dimethylaminobutanoyl)cyclohexene reacts analogously with hydrogen sulphide to form up to 78% of 2-methyl-1-thia-4-decalone.[44]

It has been shown[45] that the methiodides (XL) can be used instead of the Mannich bases. On heating to 50–60 °C in an atmosphere of nitrogen in the presence of sodium sulphide in an aqueous medium, these compounds are converted into 1-thia-4-decalones or 2-thiabicyclo[4.3.0]-5-nonanones:[45]

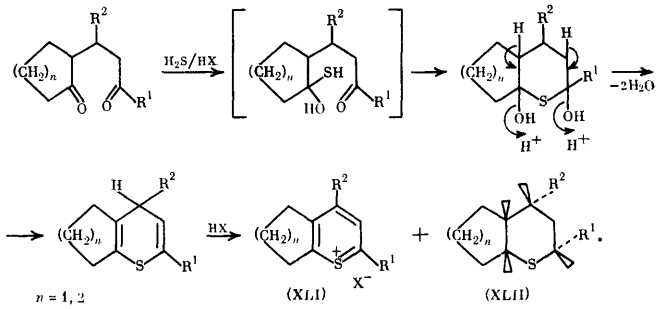


R = H, CH_3; $n = 1, 2$.

The configuration has been assigned[44,45] only for *trans*-1-thia-4-decalone.

9. Aryl-Substituted *cis*-1-Thiadecalins and 2-Thiabicyclo-[4.3.0]Nonanes

(a) *Synthesis from 1-aryl- and 1,3-diaryl-3-(2-oxocycloalkyl)-1-propanones.* The configurationally and conformationally homogeneous aryl-substituted *cis*-1-thiadecalins and 2-thiabicyclo[4.3.0]nonanes have become available as a result of the reaction of 1-aryl- and 1,3-diaryl-3-(2-oxocycloalkyl)-1-propanones with hydrogen sulphide in acid media.[46–49] On interaction with hydrogen sulphide in the presence of acids at room temperature, the 1,5-diketones ($R^1 = Ar$) undergo heterocyclisation with formation of condensed 4*H*-thiopyrans as intermediates. On treatment with protic acids (fluoroboric,[46] hydrobromic,[47,48] hydrochloric,[48] and trifluoroacetic[49]), the latter disproportionate to form the corresponding 2-aryl-5,6-polymethylenethiopyrylium salts (XLI) and 3-aryl-2-thiabicyclo[4.3.0]nonanes or 2-aryl-*cis*-1-thiadecalins (XLII, $R^1 = C_6H_5$ or $C_6H_4OCH_3$-4; $R^2 = H$; $n = 1$ or 2) in proportions of 2:1.

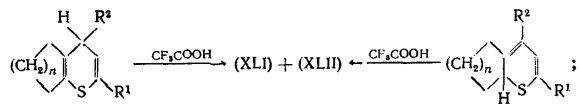


Diaryl-substituted 2-thiabicyclo[4.3.0]nonanes and *cis*-1-thiadecalins ($R^1 = C_6H_5$ or $C_6H_4OCH_3$-4; $R^2 = C_6H_5$ or $C_6H_4OCH_3$-4; $n = 1$ or 2) can be obtained from the corresponding 1,5-diketones only in trifluoroacetic acid, which functions simultaneously as the solvent and a reactant in the above reaction.[49] Complete disproportionation of the intermediate 2,4-diaryl-5,6-polymethylene-4*H*-thiopyrans is not observed in the presence of the other acids enumerated and 3,5-diaryl-2-thiabicycloalkenes, in which an angular double bond is retained, are isolated as the reaction products together with the salts.[47,48]

It has been established by ^1H and ^{13}C NMR that *cis*-1-thiadecalins having the 2α-R^1-4α-R^2-configuration are formed.[50,51] It may be that the aryl-substituted 2-thiabicyclo[4.3.0]nonanes obtained by the same method have the same configuration. Despite the fact that the yields of the required products do not exceed 30%, the presence of only one stage and stereospecificity are undoubted advantages of the method.

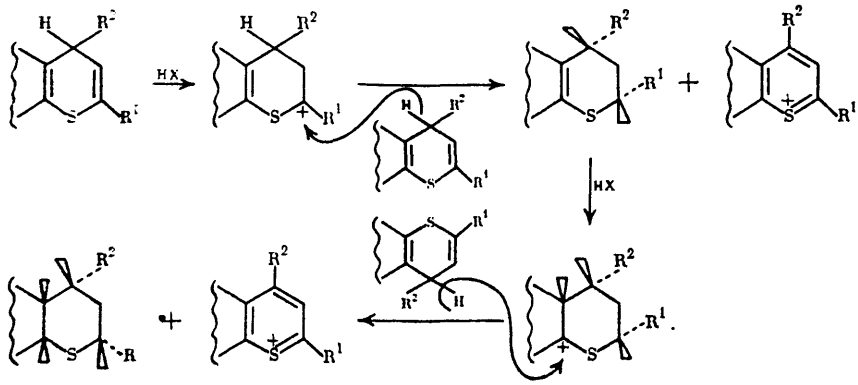
(b) *Disproportionation of 5,6-polymethylene-4H(6H)-thiopyrans and 2-thiabicycloalkenes.* The disproportionation of 5,6-polymethylene-4*H*(6*H*)-thiopyrans as a method of synthesis of condensed thiacyclohexanes can be of independent importance, since the initial compounds of the type stated can be obtained in reactions of 1,5-diketones with hydrogen sulphide in ethanol under the catalytic influence of hydrogen chloride[52] and from 5,6-polymethylenethiopyrylium salts on interaction with Grignard reagents[53] or on reduction with lithium aluminium hydride.[54,55]

2-Aryl and 2-aryl-4R-5,6-polymethylene-4*H*(6*H*)-thiopyrans disproportionate into the trifluoroacetates (XLI) and the thiacyclohexanes (XLII) in the presence of trifluoroacetic acid, which is an effective protonating and solvating agent:[51,56]



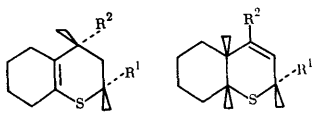
$R^1 = C_6H_5$, $C_6H_4OCH_3$-4; $R^2 = H$, C_6H_5, $C_6H_4OCH_3$-4, $C_6H_3(OCH_3)_2$-3,4, CH_3, C_2H_5, $CH_2C_6H_5$; $n = 1, 2$; $X^- = CF_3COO^-$

Thiadecalins and 2-thiabicyclo[4.3.0]nonanes arise in this reaction as a result of the ionic reduction of thiopyran with participation of a protic acid and with intermolecular transfer of a hydride ion from another thiopyran molecule to the tertiary carbonium ion generated following the protonation of the double bond of the heterocycle, as shown in the scheme below:[49,56]



The sterically less hindered double bond in the 2,3-position is reduced first in 4*H*-thiopyrans and this is followed by the reduction of the angular double bond. The same *cis*-1-thiadecalins or 2-thiabicyclo[4.4.0]nonanes are obtained from the 6*H*-isomers as from the 4*H*-isomers. The mechanism of the disproportionation of the 6*H*-isomers has been described.[56]

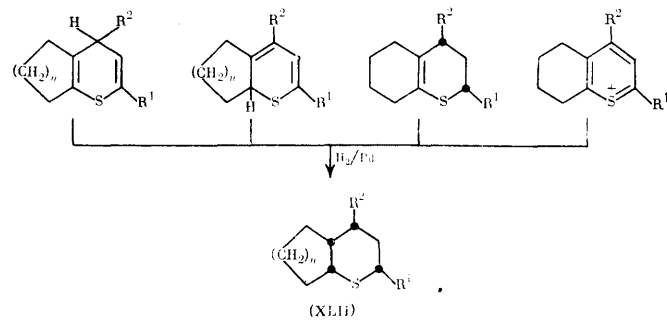
The degree of disproportionation of 5,6-polymethylene-4*H*(6*H*)-thiopyrans depends on the degree of their substitution and the nature of the protic acid. The reduction of only one double bond of the heterocycle with formation of thiabicycloalkenes is observed for the 2,4-diaryl-substituted derivatives in reactions with perchloric, hydrochloric, hydrobromic, and fluoroboric acids.[48,54]



By virtue of the hydride mobility of the α-hydrogen atoms, the condensed dihydrothiopyrans obtained in this way can also disproportionate on refluxing in trifluoroacetic acid, producing thereby thiopyrylium salts and thiacyclohexanes in proportions of 1 : 2.[57,58]

(c) *The ionic hydrogenation of 5,6-polymethylene-4H(6H)-thiopyrans and 2-thiabicyclo[4.4.0]decanes.* The reduction of the above bicyclic sulphides with trifluoroacetic acid and triethylsilane with sulphide : silane : acid ratios of 1 : 3 : 5 makes it possible to synthesise quantitatively 2α-R^1-4α-R^2-*cis*-1-thiadecalin (XLII).[51] Like disproportionation, the ionic reduction of 5,6-polymethylene-4*H*(6*H*)-thiopyrans and 2-thiabicycloalkenes gives rise to 2-thiabicycloalkanes having exclusively the *cis,cis,cis*-configuration.

(d) *The liquid-phase hydrogenation of condensed 4H(6H)-thiopyrans, dihydrothiopyrans, thiopyrylium salts, and 4H-thiopyran 1,1-dioxides.* Aryl-substituted 1-thiadecalins and 2-thiabicyclononanes of type (XLII) are formed on hydrogenation of the corresponding unsaturated heterocyclic compounds in the presence of 10% Pd/C. The *cis*-addition of hydrogen to the multiple bonds has been noted:



(XLII)

Thiopyrans and dihydrothiopyrans are hydrogenated at 100 °C at an initial hydrogen pressure of 50 atm,[48,49] while the reduction of 2,4-diphenyl-5,6-tetramethylenethiopyrylium tetrafluoroborate requires more severe conditions (a temperature of 100 °C and a hydrogen pressure of 100 atm).[60] The yields of the thiacyclohexanes (XLII) obtained from thiopyrans and dihydrothiopyrans are 75–80%, while the yields of the same compounds derived from 5,6-polymethylenethiopyrylium salts are 60%.

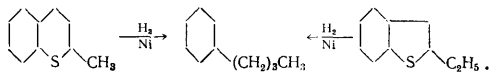
The hydrogenation of 5-oxo-2,4-diphenyl-5,6,7,8-tetrahydrothiochromene and 2,4-diphenyl-5,6-tetramethylene-4*H*-thiopyran 1,1-dioxide under the same conditions (100 °C, 50 atm) in the presence of 10% Pd/C involves the reduction of only the double bonds of the heterocycle, while the sulphonyl and carbonyl groups are unaffected.[61,62]

III. STRUCTURE AND PROPERTIES

The complexes with mercury(II) chloride, sulphoxides, sulphones, sulphimides, sulphonium salts, and ylides constitute the traditional list of derivatives of open-chain sulphides or saturated cyclic sulphides. The properties of condensed thiacyclohexanes have much in common with those

of the sulphides but any chemical reactions are very intimately related with the stereochemistry of these interesting systems. The stereochemical aspects of their study has in fact assumed a special importance in recent times.

The desulphurisation reaction in the presence of Raney nickel, which is widely used in the study of sulphides of of petroleum origin, has found hardly any applications in the chemistry of condensed thiacyclohexanes, namely as a result of the complexity of the system and the development of modern methods (^{1}H and ^{13}C NMR). The desulphurisation of condensed cyclic sulphides frequently does not even allow a conclusion concerning the size of the heterocycle[2] let alone the stereochemical features of the structure:



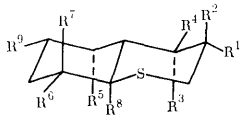
1. Complexes with Bivalent Mercury Salts

Another reaction, which has long been regarded as traditional in the study of sulphides, involves interaction with mercury salts and is used to isolate and identify thiacyclohexanes. Complexes of *cis*- and *trans*-1-thiadecalins, their alkyl derivatives, and 2-thiabicyclo[4.3.0]nonane with mercury(II) chloride, having the composition $R_2S.HgCl_2$, have been described.[21,22,24,25]

2. The Stereochemistry of *cis*- and *trans*-1-Thiadecalins

The study of the ^{13}C and ^{1}H NMR spectra of a large number of unsubstituted and methyl-substituted *cis*- and *trans*-1-thiadecalins permitted configurational and conformational assignments.[63] The signals were assigned by the method of double resonance, the parametrisation of the effects of substituents, and comparison with C- and N-analogues. The thiadecalins investigated were synthesised as described by Claus and Vierhapper.[25]

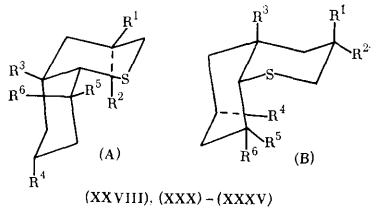
trans-1-Thiadecalins (XII)–(XX) are conformationally rigid systems for which ring inversion is ruled out. The nine expected signals have been detected in the ^{13}C NMR spectrum of *trans*-1-thiadecalin (XII). Analogous data have been obtained for methyl-substituted *trans*-1-thiadecalins. Without dwelling on the discussion of the spectra, which can be found in another communication,[63] one should note that the signals of the axial methyl groups in the spectra of the sulphides are to higher field than those of the equatorial CH_3 group. The lowest-field signals correspond to the C(9) and C(10) atoms.



(XII) – (XX)

Table 1 presents the parameters of the ^{13}C NMR spectra of unsubstituted *cis*- and *trans*-thiadecalins and some of their derivatives.[63,67,69,81,92]

At 30 °C the *cis*-1-thiadecalin (XXVIII) undergoes slow inversion, as shown by the broadening of five of the nine signals in the ^{13}C NMR spectrum. Two groups of signals are observed in the spectrum at −70 °C and can be assigned to conformers (A) and (B) (in proportions of 58:42).[63]

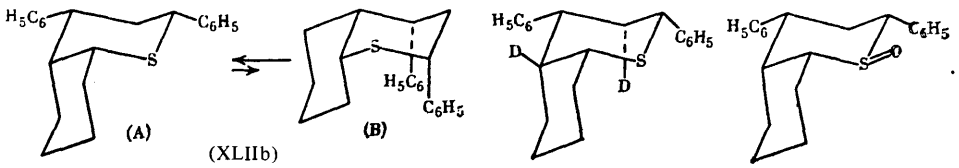


(XXVIII), (XXX) – (XXXV)

The ^{13}C NMR spectra of methyl-substituted *cis*-1-thiadecalins, namely the 3β-CH_3-derivative (XXX), the 10-CH_3-derivative (XXXII), and the 8β-CH_3-derivative (XXXV), also indicated the presence of two conformers. The conformational equilibrium has been investigated by low-temperature ^{13}C NMR.[63] Table 2 lists the ratios of the conformers, the equilibrium constants K, and the free energy differences ΔG^0.

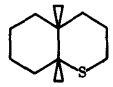
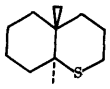
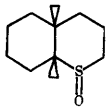
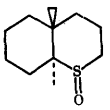
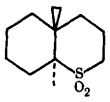
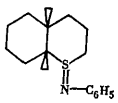
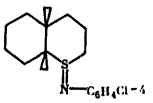
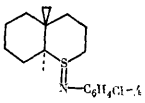
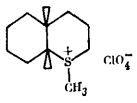
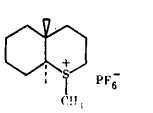
The 3α-CH_3-derivative (XXXI), the 6α-CH_3-derivative (XXXIII), and the 8α-CH_3-derivative (XXXIV) of *cis*-1-thiadecalin are conformationally homogeneous at room temperature, the first existing in the (B) conformation and the other two in the (A) conformation, in which the *syn*-axial interactions between the substituent and the methylene groups of the ring have been reduced to a minimum. For example, the (B) conformation is ruled out for the sulphide (XXXIV) by two *syn*-axial interactions of the CH_3 group with C(2) and C(4); in contrast to this, in the (A) conformation there is only one *gauche*-interaction of the CH_3 group in the heteroatom.

The configurational and conformational assignments for 2,4-diphenyl-1-thiadecalin, obtained as described in a number of communications,[49,56,59] have been made on the basis of the ^{1}H NMR study (80 MHz) of the disulphide itself, its 3,10-dideuterio-derivative, and the 1-oxide in the presence of $Eu(dpm)_3$.[50] It has been established that the disulphide has the *cis,cis,cis*-configuration and exists in the (A) conformation owing to the destabilisation of the other conformer by the *syn*-axial interaction of the phenyl groups with one another and with C(6) and C(8).



(XLIIb)

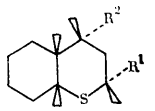
Table 1. ^{13}C NMR parameters of *cis*- and *trans*-1-thiadecalins and some derivatives in $CDCl_3$.

Compounds	Configuration and conformation*	T, °C	Chemical shifts δ, p.p.m.**									Refs.
			C (2)	C (3)	C (4)	C (5)	C (6)	C (7)	C (8)	C (9)	C (10)	
	*cis*-A *cis*-B	−70 −70	29.92 23.59	21.10 28.28	32.50 24 92	24.40 34.22	26.69 19.61	28.88 28.28	31.86 27.34	43.11 40.41	36.01 36.75	[63]
	*trans*-	30	30.04	28.23	34.40	34.56	26.34	26.76	32.58	47.01	44.27	[63]
	*cis*-A (β) *cis*-B (β)	−50 −50	51.48 40.25	19.09 15.68	31.22 25.90	25.25 32.11	27.36 20.46	20.63 27.36	26.20 21.48	64.65 56.22	38.72 23.40	[67]
	*trans*-(β) *trans*-(α)	+30 +30	46.45 51.47	15.71 21.75	32.89 32.89	33 84 33.14	25.53 25.39	26.06 25.45	27.74 27.01	59.57 67.11	31.27 38.74	[69]
	*trans*-	+30	51.59	23.15	32.06	32.78	24 78	25.17	20.29	65.06	39 83	[69]
	*cis*-A (β)	−45	48.44	19.95	30.80	(25.54)	27.13	21.19	(25.96)	63.57	32.23	[67]
	*cis*-B (α) *cis*-A, B (β) *cis*-A	30 30 −69	38.80 47.79 48.04	(23.36) 19.70 19.32	(23.07) 30.34 30.60	32.56 25 61 (25.53)	20.78 27.97 26.97	25.95 21.81 21.16	16.34 25.61 (25.79)	54.37 63.25 63.84	35.38 37.44 38.05	[81]
	*trans*-(α) *trans*-(β)	30 30	48.55 43.67	22.94 16.49	32.37 32.66	33.34 34.07	(25.54) (25.86)	(25.28) (25.24)	27.62 28.11	66.55 59.46	40.03 31.75	[81]
	*cis*-B (α) *cis*-A (β) *cis*-B (β)	+70 −68 −68	34.38 40.00 29.82	23.45 18.29 18.12	23.85 29.82 22.10	33.59 (25.75) 32.55	19.47 (25.94) 19.67	26.43 20.91 26.77	20.27 26.77 24.47	49.48 57.13 48.49	35.97 36.41 27.93	[92]
	*trans*-(α) *trans*-(β)	−30 +30	41.32 36.41	23.35 16.10	31.84 30.80	33.82 33.94	(25.48) (25.43)	(25.81) (26.75)	28.52 28.69	58.83 52.50	40.30 34.42	[92]

*β denotes that the substituent is located on the same side of the ring as the carbon atom at C(10) and α denotes that it is located on the opposite side of the ring relative to the hydrogen atom at C(10).
**The chemical shifts whose assignment is tentative are given in brackets.

In order to establish the configurations and preferential conformations, a study has been made of the ^{13}C NMR spectra at room temperature for 2-aryl- and 2,4-diaryl-1-thiadecalins (XLII) obtained in the disproportionation reactions and as a result of the ionic hydrogenation of condensed 2-aryl- and 2,4-diaryl-5,6-tetramethylene-4*H*(6*H*)-thiopyrans and the corresponding dihydrothiopyrans and also as a result of their hydrogenation. The signals were assigned with the

aid of spectra with incomplete decoupling from the protons and by comparing the experimental and theoretical spectra; the latter were calculated using the known parameters of the ^{13}C NMR spectra of unsubstituted *cis*- and *trans*-1-thiadecalins[63] and the increments for the equatorial phenyl group in the substituted cyclohexane.[64]



(XLII)

(a) $R^1 = C_6H_5$, $R^2 = H$; (b) $R^1 = R^2 = C_6H_5$; (c) $R^1 = C_6H_5$, $R^2 = C_6H_3OCH_3$-4; (d) $R^1 = C_6H_3OCH_3$-4, $R^2 = C_6H_5$; (e) $R^1 = C_6H_5$, $R^2 = C_6H_3(OCH_3)_2$-3,4

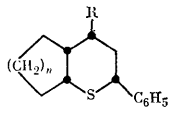
Table 2. Conformational transitions in mobile *cis*-1-thiadecalins*.[63]

Compound	(A), %	(B), %	K	ΔG^0, kcal mol^{-1}
cis-1-Thiadecalin (XXVIII)	58	42	1.4	+0.14
3β-Methyl-*cis*-1-thiadecalin (XXX)	95	5	19	+1.2
10-Methyl-*cis*-1-thiadecalin (XXXII)	33	67	0.49	−0.29
8β-Methyl-*cis*-1-thiadecalin (XXXV)	17	83	0.23	−0.65

*In $CHCl_3$ at −68 °C.

Compounds (XLII, a–e) belong to the *cis*-1-thiadecalin series. They all have the 2α-R^1-4α-R^2-configuration at C(2) and C(4) and are distinguished by a conformational rigidity, as already noted above for the sulphide (XLIIb).[50,51]

The dipole moments of certain aryl-substituted *cis*-1-thiadecalins (XLII, a, b, and e) and also 2-thiabicyclo[4.3.0]-nonanes (XLIIf, R = H) and (XLIIg, R = C_6H_5), measured by the Debye method in benzene at 20 °C, have been published.[65] The dipole moments vary from 1.51–1.96 D:



(XLII, a, b, e–g)

R	n	μ, D	n	μ, D
H	1	1.63	2	1.91
C_6H_5	1	1.51	2	1.82
$C_6H_3(OCH_3)_2$-3,4	—	—	2	1.96

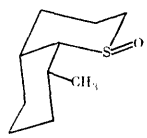
The scheme shows that the dipole moments of the corresponding 2-thiabicyclo [4.3.0]nonanes are smaller by 0.28–0.31 D than those of the *cis*-1-thiadecalins with the same substituents. On the other hand, a slight decrease (0.008 D) has been noted on passing from saturated systems to 5,6-polymethylene-4*H*-thiopyrans, which may be an indication of the equatorial position of the substituent. This is consistent with the structure of the aryl-substituted *cis*-1-thiadecalins (XLII, a–e) (with the aryl group in the equatorial position) and suggests that the aryl-substituted 2-thiabicyclo[4.3.0]nonanes have an analogous structure.

3. Sulphones and Sulphoxides

(a) *Methods of synthesis.* Certain sulphones have already been described above in the discussion of the methods of synthesis, since their formation uses sulphonyl-containing compounds as the starting materials for the synthesis of the heterocyclic system. The oxidation of condensed thiacyclohexanes, like that of thianes, results in the formation of *S*-oxides or, in the presence of an excess of the oxidant, of *SS*-dioxides. The oxidants employed are hydrogen peroxide,[21,22,24,38,66] *m*-chloroperbenzoic acid,[25,67] and t-pentyl hydroperoxide in the presence of MoCl or $Mo(CO)_6$.[68] The sulphones of 1-thiadecalin,[21,69] 4-methyl-1-thiadecalin,[22] 2-thiabicyclo[4.3.0]nonane,[24] 4-hydroxy-2-methyl-1-thiadecalin,[68] 2-methyl-1-thiadecalin,[68] 3-aryl- and 3,5-diaryl-2-thiabicyclo[4.3.0]nonanes,[59] and 2-aryl- and 2,4-diaryl-*cis*-1-thiadecalins[59] and the sulphoxides of 2-methyl-1-thiadecalins,[38,68] 6-methyl- and 8-methyl-*cis*-1-thiadecalins,[25] and 2-aryl- and 2,4-diaryl-*cis*-thiadecalins[49] have been described in the literature.

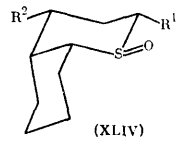
The sulphoxides with the α- and β-configurations are obtained in 55% yield by the oxidation of *trans*-1-decalin with a calculated amount of *m*-chloroperbenzoic acid.[69] A 79 : 21 mixture of the diastereoisomeric *cis*-1-thiadecalin 1-oxides with the α- and β-configurations is formed under identical conditions. The pure *cis*-1-thiadecalin 1β-oxide has been isolated by crystallising the crude product from an ether–petroleum ether mixture (yield 56%).[67]

The oxidation with *m*-chloroperbenzoic acid of the conformationally rigid 6α-methyl-*cis*-1-thiadecalin (XXXIII) and 8α-methyl-*cis*-1-thiadecalin (XXXIV), which exist in the (A) conformation,[63] leads solely to the β-sulphoxides in yields up to 90%, while the formation of the α-sulphoxides is ruled out by the powerful *syn*-axial interaction,[25,63] for example:



(XLIII) $S\alpha-CH_3$.

The formation of the sulphoxide having the β-configuration (with an equatorial S–O bond) is observed in the oxidation of the conformationally rigid 2α, 4α-diphenyl-*cis*-1-thiadecalin (XLIIb) with a calculated amount of hydrogen peroxide.[50] The sulphoxides (XLIV, a–d) have been obtained analogously and, although the configuration of the sulphur atom has not been assigned, one can state with confidence that the sulphinyl group in these compounds is equatorial:[49]

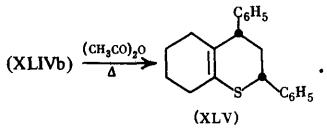


(XLIV)

(a) $R^1 = C_6H_5$, $R^2 = H$; (b) $R^1 = R^2 = C_6H_5$; (c) $R^1 = C_6H_5$, $R^2 = C_6H_4OCH_3$-4; (d) $R^1 = C_6H_4OCH_3$-4, $R^2 = C_6H_5$.

(b) *The Pummerer rearrangement.* Refluxing of 2α, 4α-diphenyl-*cis*-1-thiadecalin 1-oxide (XLIVb) in acetic anhydride under the conditions of the Pummerer reaction

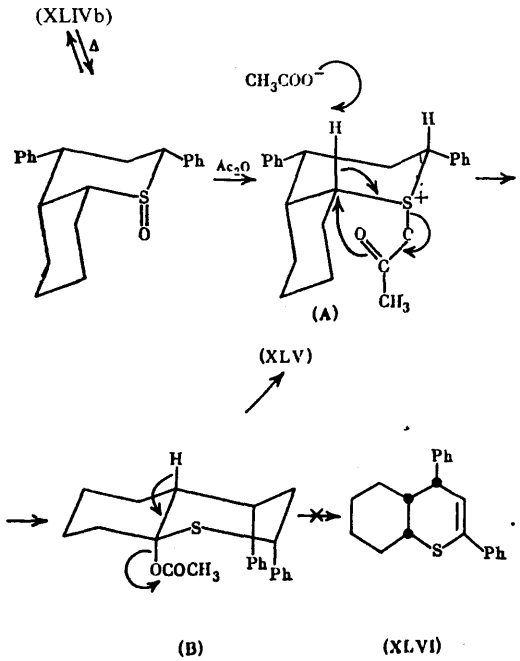
leads to the formation of *cis*-3,5-diphenyl-2-thiabicyclo[4.4.0]-$\Delta^{1,6}$-decane (XLV) as the product of the rearrangement: [70]



(XLV)

The structure of the sulphide (XLV) has been established by X-ray diffraction analysis (XDA). Both phenyl substituents occupy equatorial positions. Both rings have the distorted half-chair conformation. [70]

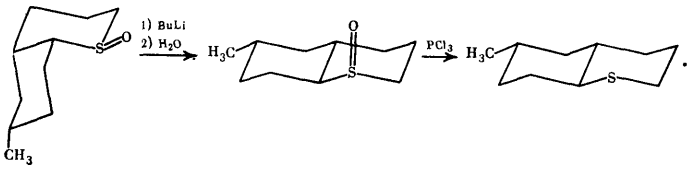
According to the generally accepted mechanism of the rearrangement of acyclic sulphoxides, the second of the two stages (*O*-acylation and deprotonation) is rate-limiting, the ylide formed being stabilised by the 3*d* orbital of the sulphur atom and being attacked by an external acetate anion. Despite the more acid character of the hydrogen atom at C(2) in the onium intermediate (A), the formation of *cis*,*cis*-3,5-diphenyl-2-thiabicyclo[4.4.0]dec-3-ene (XLVI) is not observed in the rearrangement of the sulphoxide (XLIVb):



This justifies the hypothesis that the rearrangement of the onium intermediate (A) to the 9-acetoxy-derivative (B) probably proceeds intramolecularly, as shown in the scheme, and leads to the final product (XLV) via *trans*-elimination. The absence of the isomer (XLVI) from the reaction products shows that the substituents at C(2) offers steric hindrance to the formation of the 2-acetoxy-derivative and hence of the isomer (XLVI).

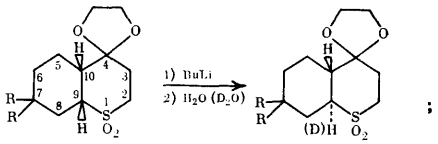
3-Methyl-2-thiabicyclo[4.4.0]dec-3-ene has been obtained under the conditions of the Pummerer rearrangement from a mixture of the four isomeric 2-methyl-1-thiadecalin 1-oxides, with 2β-methyl-*trans*-1-thiadecalins 1-oxide (89%) and 2α-methyl-*trans*-1-thiadecalin 1-oxide (7%) predominating, which should also be accounted for by the sensitivity of the reaction to steric factors. [71]

(c) *The CH-acid properties of sulphones and sulphoxides.* The *cis*,*trans*-isomerisation of sulphones and sulphoxides in the presence of BuLi and the subsequent reduction of the SO group by PCl_3 are used to obtain, for example, 6α-methyl-*trans*-1-thiadecalin, which is obtained in a low yield by other methods: [25,63]

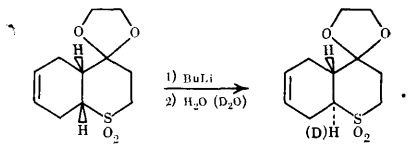


Calculations have shown that the *trans*-isomers of this sulphoxide are more stabel than the *cis*-isomers to the extent of 1.7 kcal mol^{-1}. [72] Their sulphoxide group is axial, as in thian 1-oxides. [73,74] Deuterio-derivatives, for example 9-methyl-*trans*-1-thiadecalin-2,2-d_2-1-oxide, can be obtained by the successive treatment of the sulphoxides with butyllithium and D_2O. [25]

The stereochemistry of the metallation of *cis*-sulphones (XLVIIa, R = H), (XLVIIb, $R_2 = OCH_2CH_2O$), and (XLVIII) by treatment with n-butyl-lithium in benzene at the normal temperature has been investigated. Hydrolysis of lithiosulphones leads to the *trans*-isomers (XLIX) and (L): [43,75]

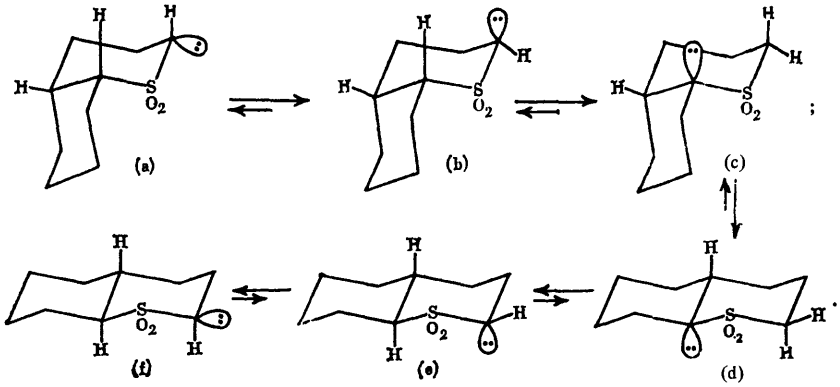


(XLVII a and b) (XLIX, a and b)



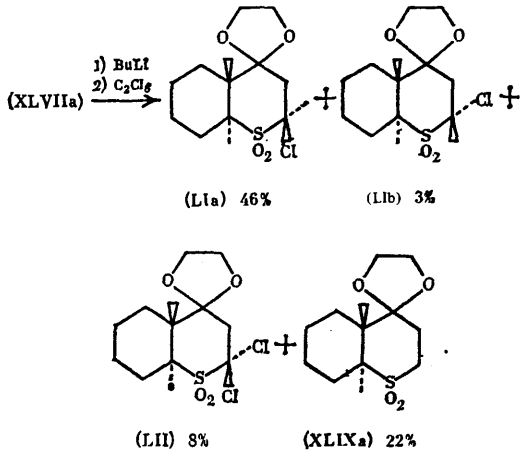
(XLVIII) (L)

The *cis*,*trans*-isomerisation, which involves the inversion of the configuration at C(9), is an intramolecular process, as shown by investigating the reaction using different reactant ratios. The structure of the final products has been confirmed by ^1H and ^{13}C NMR. It has been suggested, [43,75] that BuLi attacks the equatorial hydrogen atom at C(2), the α-sulphonyl carbanion (a) being in equilibrium with the anion (b) having the inverted configuration. Intramolecular proton transfer leads to the anion (c), which is converted into the anion (f) by proton shifts.



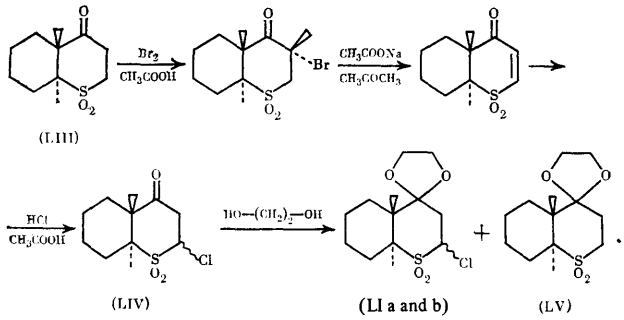
Refluxing of the sulphones (XLVII) and (XLVIII) with NaOD in a D_2O–dioxan mixture for 12 h yields trideuteriated sulphones with retention of the configuration at C(9), which can be explained by the short lifetime of the sulphonyl carbanion in a protic medium compared with the rate of inversion.[43] The mild conditions of the exchange (pH 8.5) in the experiment with the sulphone (XLVIIa) lead to the exchange of only the equatorial H(2) atom, which can be inferred from the disappearance of its signal (δ = 2.87) in the ^{1}H NMR spectrum. This is the first demonstration of a difference between the kinetic acidities of the equatorial and axial hydrogen atoms at C(2) in sulphones of type (XLVII).[43]

Chlorination of the lithiosulphonyl carbanions obtained from the *cis*-sulphone (XLVIIa) with hexachloroethane leads to a mixture of the *trans*-sulphones (LI, a and b), (LII), and (XLIXa). Products containing chlorine at C(9) were not detected:[75]



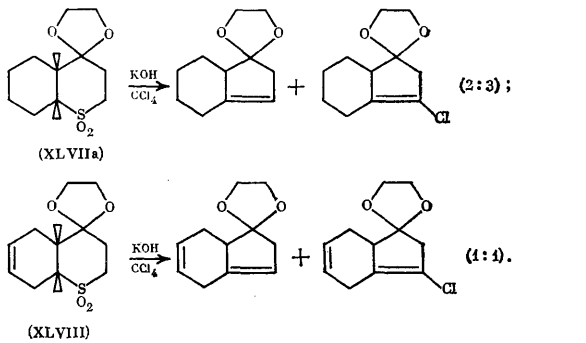
The sulphones (XLVIIb) and (XLVIII) behave analogously under the conditions indicated.

The *trans*-1-thiadecalone 1,1-dioxide (LIII) can be converted into the diastereoisomeric 2-chloro-*trans*-4-thiadecalone 1,1-dioxide (LIV) and further into the acetals (LI, a and b) in accordance with the scheme:



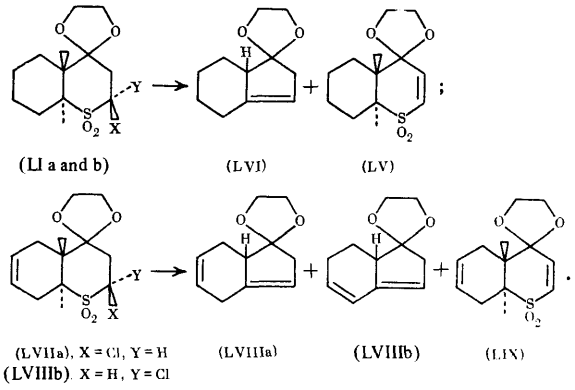
The chloro-derivatives (LI, a and b) are obtained in these reactions in low yields, which makes it preferable to halogenate the lithio-derivatives.[75] In addition, the formation of a considerable amount of the elimination products (LV) has been noted.

(d) *The Ramberg–Bäcklund reaction.* 4,4-Ethylenedioxy-*cis*-1-thiadecalin 1,1-dioxide (XLVIIa) and its unsaturated analogue (XLVIII) are converted via the Ramberg–Bäcklund reaction on treatment with KOH/CCl_4 into the acetals of hydrindenone and their chloro-derivatives:[76]



In the interaction of the α-halogenosulphones (LI, a and b) and (LVII) having the *trans*-configuration with potassium (sodium) t-butyloxide, the Ramberg–Bäcklund reaction can

compete with the 1,2-elimination of the hydrogen halide.[77] The more polar dimethyl sulphoxide (DMSO) favours the Ramberg–Bäcklund reaction while in the less polar dimethoxyethane (DME) the 1,2-elimination reaction predominates. It has been shown that the *trans*-sulphone (LVIIa) gives rise preferentially to the dienes (LVIIIa) and (LVIIIb), the latter as a result of the allyl rearrangement:[77]

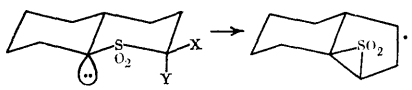


(LI a and b) (LVI) (LV)

(LVIIa), X = Cl, Y = H (LVIIIa) (LVIIIb) (LIX)
(LVIIIb), X = H, Y = Cl

The epimers of the *trans*-sulphones (LVII, a and b) behave differently in the reaction with potassium t-butoxide in DME: the isomer (LVIIa) with an equatorial halogen atom gives rise to the dienes (LVIII, a and b) while the isomer (LVIIb) with an axial halogen atom undergoes 1,2-elimination with formation of the vinyl sulphone (LIX).

It has been established[77] that the Ramberg–Bäcklund reaction, leading to an olefin, proceeds in the case of the *trans*-sulphones with the halogen in the equatorial position (X = Cl, Y = H) via the *Z*-episulphone (the sulphonyl group has the *Z*-configuration in relation to the angular hydrogen atom):

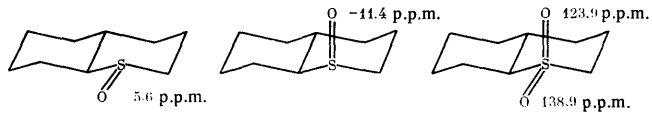


In conclusion one should note that the *cis*-configuration of the initial sulphone is more favourable for the Ramberg–Bäcklund reaction than the *trans*-configuration.[76,77]

(e) *The ^{13}C and ^{17}O NMR spectra of the sulphoxides and sulphones.* The study of the ^{13}C NMR spectrum of *cis*-1-thiadecalin 1β-oxide showed that it exists predominantly (to the extent of 65%) in the equatorial conformation.[67]

The ^{13}C NMR spectra of the 1α-oxide, 1β-oxide, and 1,1-dioxide of *trans*-1-thiadecalin have been described in a communication[69] which discusses the influence of the sulphinyl and sulphonyl groups on the chemical shifts of the carbon atoms (C_β and C_γ). The assignment of the signals to the axial and equatorial conformations of the diasteroisomeric sulphoxides has been based on the difference between the chemical shift of the C_β and C_γ atoms. Thus, of the two diastereoisomeric *trans*-1-thiadecalin 1-oxides, the isomers with the highest-field C_γ shift and the least low-field C_β shift have been assigned to the β-configuration (the S–O bond is axial) (Table 1). Compared with *trans*-1-thiadecalin, the introduction of the sulphonyl group into the molecule leads to the deshielding of the carbon atoms in the β-position [C(3) and C(9)], which can be explained by the influence of the inductive effect of the partially positively charged sulphur atom in the SO group and the β-effect of the oxygen substituent at the sulphur atom.[69]

The ^{17}O NMR spectra of the sulphoxides and the sulphone of *trans*-1-thiadecalin have been investigated. The β-isomer with the axial sulphinyl oxygen atom gives rise to a signal to a higher field than the α-isomer with an equatorial SO group ($\Delta\delta$ = 17 p.p.m.), which constitutes confirmation of the shielding by the γ-*gauche*-interaction with a CH_2 group:[78]

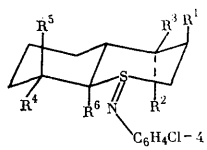


The scheme shows that the sulphonyl oxygen atoms are very highly deshielded compared with the sulphinyl oxygen atoms. The signal of the axial oxygen atom (δ = 123.9 p.p.m.) is in a higher field than the signal of the equatorial atom (δ = 138.9 p.p.m.).[78]

4. The *cis*- and *trans*-1-Thiadecalin 1-*N*-Arylimides

(a) *The synthesis of cis- and trans-1-thiadecalin 1-N-arylimides.* Sulphimides are a new class of thiadecalin derivatives. They can be regarded as isoelectronic analogues of sulphoxides. The methods of their synthesis, the mechanisms of their formation, and their structure and chemical properties have been described.[79–82] The reactions of the *cis*- and *trans*-1-thiadecalins with 4-chloroaniline and a slight excess of *N*-chlorosuccinimide (NCS) or t-butyl hypochlorite lead to the formation of the configurationally homogeneous crystalline *N*-4-chlorophenylsuphimides.[79,80] The sulphimides can be obtained also from the sulphoxides by treatment with P_2O_5 and 4-chloroaniline.[80] The configuration and the preferred conformation (in the case of mobile systems) in the series of *cis*- and *trans*-1-thiadecalin 1-*N*-4-chlorophenylimides have been determined by ^1H and ^{13}C NMR.[81]

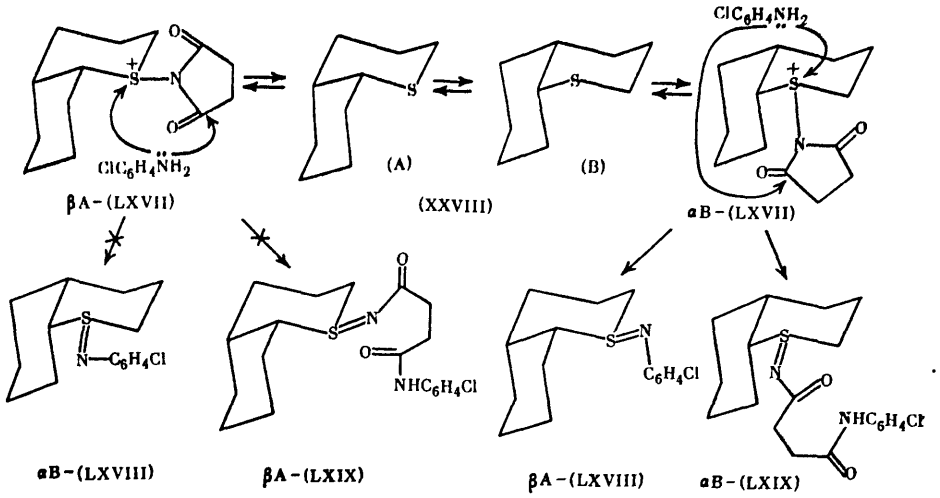
The sulphimides (LX)–(LXVI), having the α-configuration and an equatorial SN bond, have been found to form in the reactions of the *trans*-1-thiadecalins (XII), (XIV)–(XVI), and (XVIII)–(XX) with 4-chloroaniline and NCS or t-butyl hypochlorite.[79–80] The sulphimide α-(LXIV) has been obtained even from 8α-methyl-*trans*-1-thiadecalin (XVIII) despite the unfavourable mutual disposition of the equatorial methyl group and the SN bond.[80]



α-(LX) – α-(LXVI)

(LX): all R = H; (LXI): $R^1 = 3\beta\text{-}CH_3$; (LXII): $R^2 = 4\alpha\text{-}CH_3$; (LXIII): $R^3 = 4\beta\text{-}CH_3$; (LXIV): $R^4 = 8\alpha\text{-}CH_3$; (LXV): $R^5 = 8\beta\text{-}CH_3$; (LXVI): R^6 = 9-CH_3

The conformationally mobile *cis*-1-thiadecalin (XXVIII) reacts with 4-chloroaniline and NCS to form only the sulphimide β-(XLVIII), mainly in the (A) conformation, and the ring-opening product αB-(LXIX) with the α-configuration at the sulphur atom.[79,80] The proposed reaction mechanism is presented below taking into account the preferred conformations of the reaction products:

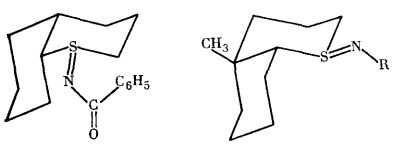


The corresponding succinimidylsulphonium chlorides are probably formed as intermediates. The substitution of the succinimidyl group in αB-(LXVII) by 4-chloroaniline takes place with inversion at the sulphur atom and leads to the sulphimide βA-(LXVIII); the product αB(LXIX) is formed from the same azasulphonium salt in a third reaction when the succinimidyl ring is opened as a result of attack on the carbonyl group, the configuration at the sulphur atom remaining unchanged.[80] The axial attack by 4-chloroaniline on the sulphur atom in the intermediate αB-(LXVII) may be facilitated by the capacity of the compound for inversion in the transition state.

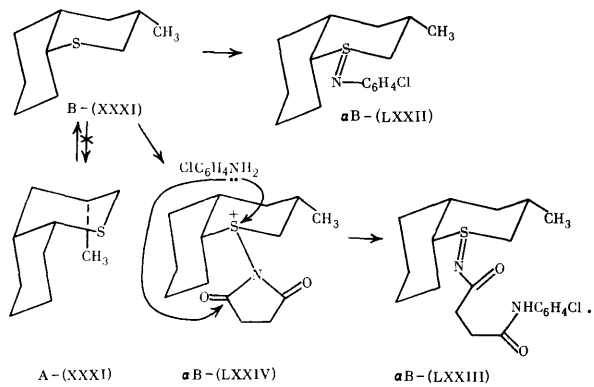
The absence of compounds αB-(LXVIII) and βA-(LXIX) from the reaction products has been explained[80] by the fact that the axial attack in the intermediate βA-(LXVII) should be hindered by the interaction with the methylene groups of the cyclohexane ring [C(5) and C(7)] and the counterion can also give rise to some hindrance. The hypothesis that azasulphonium salts may be formed in the reaction is based on the fact that the dimethyl sulphide and NCS give rise to a crystalline succinimidylsulphonium chloride.[83] Their formation is also indicated by open-chain products of the type of αB-(LXIX), which have been detected in amounts up to 30% in the analogous reactions of methyl-substituted *cis*-1-thiadecalins.

However, the results cannot be satisfactorily explained in terms of the mechanism described in all cases. Thus the reaction of *cis*-1-thiadecalin with *N*-bromobenzamide results in the formation of only benzoyl imide with the α-configuration [αB-(LXX)].

The reaction of 10-methyl-*cis*-1-thiadecalin with 4-chloroaniline/NCS or *N*-bromobenzamide yields in both cases the products (LXXI) with the β-configuration in the (A) conformation, although the initial sulphide itself exists in the (B) conformation to the extent of 67% (at −70 °C):[80]

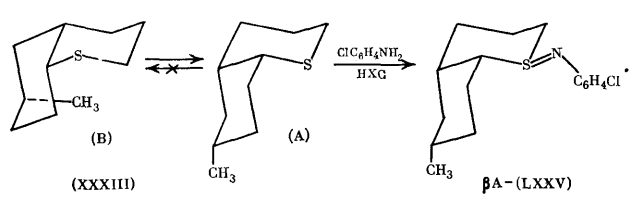


The analogous reaction of 3α-methyl-*cis*-1-thiadecalin (XXXI) led to the isolation of the imide αB-(LXXII) and the products of the ring opening in succinimide αB-(LXXIII) in high yields:[80]

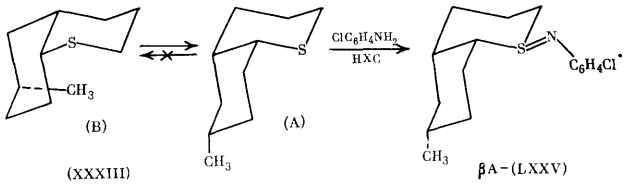


The axial attack on the intermediate αB-(LXXIV) should have led to the β-sulphimide in the (B) conformation with an axial SN bond, because ring inversion in the (A) conformation is prohibited by the *syn*-axial interaction between the CH_3 group and C(5). This attack is evidently less favourable than the competing attack on the azasulphonium salt αB-(LXXIV) at the carbonyl group, which results in the formation of the open-chain product αB-(LXXIII). The formation of the sulphimide αB-(LXXII) must be accounted for differently.

The sulphimide with the βA-(LXXV) configuration is formed in a high yield from 6α-methyl-*cis*-1-thiadecalin (XXXIII) for which ring inversion is forbidden by the *syn*-axial interaction between the methyl group and C(4):[80]



The sulphimide βA-(LXXVI) is obtained in a very low yield from 8α-methyl-*cis*-1-thiadecalins (XXXIV) for which the (A) conformation is preferred by virtue of the strong *syn*-axial interaction between the methyl group and C(2) and C(4):[80]

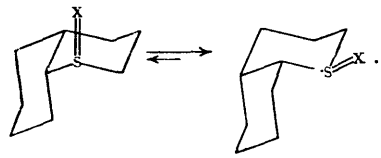


The facts described above do not make it possible to formulate a unique view concerning the mechanism of the formation of sulphimides in the reactions of thiadecalins with 4-chloroaniline and NCS examined above. As shown above, the reactions with alkyl-substituted *cis*-1-thiadecalin are sensitive to changes in the steric requirements and proceed differently with conformationally mobile and conformationally rigid sulphides. In the case of the conformationlly mobile compounds the reaction probably proceeds via the succinimidylsulphonium salts with the subsequent substitution of the succinimidyl component with inversion at the sulphur atom. It has been suggested that the sulphimides with conformationally rigid systems are formed with participation of *N*-chloroaniline, which rapidly reacts with the sulphides, removing them from the equilibrium mixture containing the sulphide, NCS, and the azasulphonium salt. The interaction of conformationally homogeneous *cis*-1-thiadecalins with 4-chloroaniline and t-butyl hypochlorite leads exclusively to sulphimides with an equatorial SN bond.[80] It has been suggested that the reaction in the presence of t-butyl hypochlorite also proceeds via *N*-chloroaniline. However, it is difficult to find a satisfactory explanation why the unsubstituted *cis*-1-thiadecalin (XXVIII) gives rise in this case to sulphimides having the α- and β-configurations in proportions of 1:2, while the reaction with NCS results in the formation of only the β-sulphimide [βA-(LXVIII)]. Finally, the reaction with *N*-bromobenzamide results in the formation of the α-benzoyl imide αB-(LXX).[79,80] The lack of data concerning the pyramidal inversion in *N*-arylsulphimides makes it impossible to infer whether the barrier to inversion is sufficiently low for the latter to play an appreciable role. However, according to the authors,[79,80] the isomerisation reactions accompanying the formation of the SN bond and leading to thermodynamically more stable products should be taken into account.

In contrast to the oxidation of thians to sulphoxides, where both isomers can be synthesised in an almost pure form or as a mixture depending on the oxidant and the oxidation conditions, the formation of sulphimide with an axial SN bond is difficult.[73] On the other hand the inversion of the configuration at the sulphur atom is known to occur in reactions of sulphoxides with arenesulphonylamides.[84,85]

A sulphimide with an axial SN bond has been obtained from *trans*-1-thiadecalin 1α-oxide with an equatorial SO bond on treatment with P_2O_5 and 4-chloroaniline (yield 10%).[80] The low yield of the reaction product can be explained by the fact that the axial attack by 4-chloroaniline on the sulphur atom in the intermediate formed from the sulphoxide and P_2O_5 is again difficult and the formation of a sulphide with an axial SN bond is an unfavourable process.[80]

(b) *The conformational equilibrium.* The conformational equilibrium for *N*-arylsulphimides and the sulphoxide of *cis*-1-thiadecalin has been investigated by the method of low-temperature ^{13}C NMR. The ratio of the equatorial (e) and axial conformers and the difference between their energies ΔG^0 have been determined.[67] The sulphoxide and sulphimides exist preferentially in the equatorial conformation:



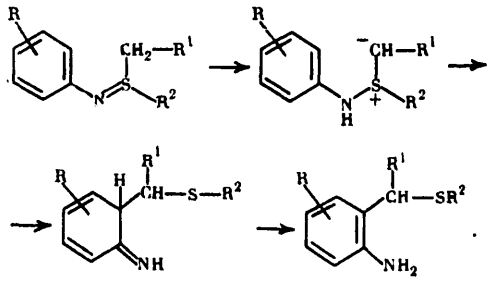
	(*e*), %	ΔG^0, kcal mol^{-1}
X = O	65	0.27
X = NC_6H_4Cl-4	>95	1.3
X = NC_6H_5	>95	1.3

A multiplicity of factors influence the observed conformational equilibrium: the *syn*-axial interactions between the axial substituent at the sulphur atom and the hydrogen atoms at C(3) and C(5), the *gauche*-interactions between the S=X group and the α-hydrogen atoms, the length of the S=X bond, the size of the heteroatom, and the polarity of the bond. At the same time, the interaction in one of the (B) conformations between the methylene groups at C(2) and C(8) is significant in *cis*-1-thiadecalin and its derivatives, which is responsible for some predominance of the (A) conformation in unsubstituted *cis*-1-thiadecalin. In contrast to thian 1-oxide, in which the SO group is preferentially axial, *cis*-1-thiadecalins 1β-oxide exists, as shown above, preferentially in the equatorial conformation, where the unfavourable interaction between C(2) and C(8) is ruled out. The above results for *cis*-1-thiadecalin 1β-oxide, *cis*-1-thiadecalin 1β-*N*-(4-chlorophenyl)imide, and the analogous 1β-*N*-phenylimide do not reveal an appreciable steric *gauche*-interaction of the substituent at the sulphur atom with the α-hydrogen atoms, and indicate at the same time the influence of the polarisation of the SX bond. In the axial conformation the SX group (X = O or N–R) is in the *gauche*-position relative to two C–C and two C–H bonds, while in the equatorial form the SX group is in the *gauche*-position relative to four C–H bonds. The dipole moments induced in these bonds by the S–X dipole should entail an increase of the fraction of the axial conformation with increase of the polarisation of the SX group by virtue of the higher polarisability of the C–C bond. Claus et al.[67] find this explanation to be the most correct.

(c) *The rearrangement of cis- and trans-1-thiadecalin 1-N-arylimides to 2-aryl-1-thiadecalins.* The configurationally and conformationally homogeneous *cis*- and *trans*-1-thiadecalin 1-*N*-(4-chlorophenyl)imides are capable of rearranging to the corresponding 2-(2-amino-5-chlorophenyl)-1-thiadecalins. The configurational assignments for the rearrangement products have been made by means of ^1H NMR.[82]

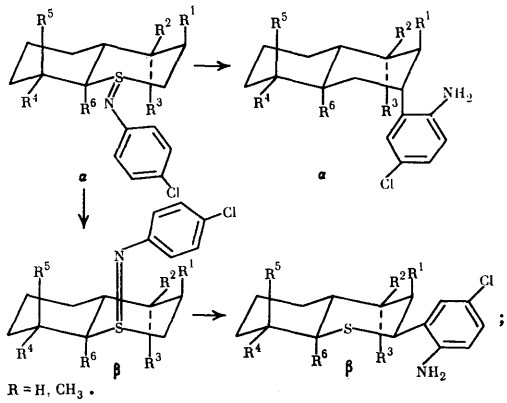
It is known[86–90] that the rearrangement of acyclic sulphimides proceeds via the azasulphonium ylide, which arises as a result of proton transfer to the nitrogen atom. This ylide is converted into cyclohexadienone imine and subsequently into the reaction product via the [2,3]-sigmatropic rearrangement. It has been shown that the rate of the

rearrangement is much higher than the rate of proton transfer:[82]



The rearrangement of 1-thiadecalin 1-*N*-arylimides proceeds with more difficulty than for the open-chain sulphimides and requires more severe conditions (heating in triethanolamine at 100–200 °C).[82] In the series of thiadecalins which are not sterically hindered the rearrangement proceeds with a high degree of stereoselectivity (>95%): sulphimides with an equatorial SN bond give rise to the rearrangement product with an axial aryl substituent, while sulphimides with an axial SN bond give rise to products with an equatorial aryl substituent. The results of the investigation confirm that the rearrangement proceeds via a cyclic transition state.

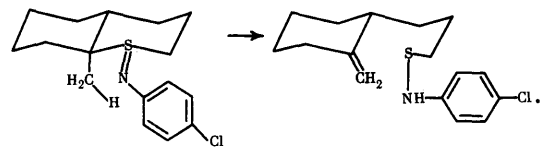
2α-Aryl-*trans*-1-thiadecalins are formed as the main products from the rigid *trans*-1-thiadecalin 1α-imides (with an equatorial bond) together with a smaller amount (<5%) of the 2β-isomers. With increase of the reaction temperature from 100° to 200 °C, the amount of the 2β-isomers increases to 25% (relative to the overall yield).



R = H, CH_3.

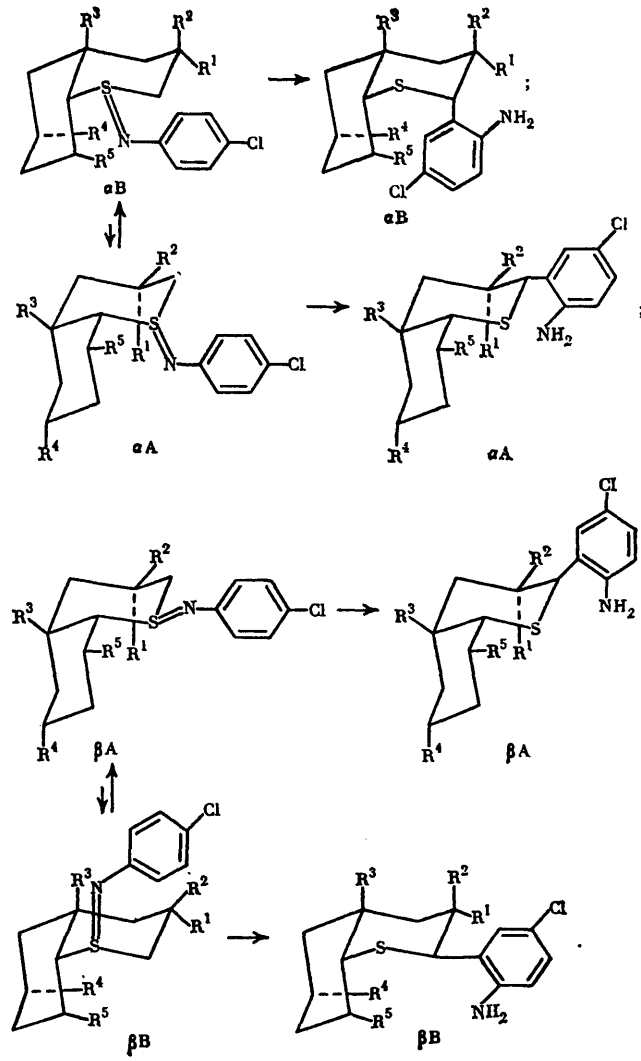
The mechanism of the rearrangement is analogous in broad outline to that of the rearrangement of acyclic sulphimides. However, the cyclic transition state in the formation of 2α-aryl-*trans*-1-thiadecalins from the 1α-imides is undoubtedly attained with more difficulty by virtue of the rigidity of the system and is more strained owing to the steric interaction between the axial hydrogen atoms at C(4) and C(9).[82] This should lead to an increase of the barrier to the rearrangement of the 1α-imide to 2α-aryl-1-thiadecalin compared with the flexible thiacyclohexane imides. In order to explain the formation of 2β-aryl-1-thiadecalines in the reactions considered one must assume the possibility of the inversion 1α-imide ⇌ 1β-imide, the inversion barrier being evidently comparable to the rearrangement barrier. It has been shown that the 1β-imide rearranges more readily to 2β-aryl-*trans*-1-thiadecalin.[82]

An unstable sulphenamide has been obtained from 9-methyl-*trans*-1-thiadecalin 1α-*N*-arylimide on heating in triethanolamine. The methyl group at C(9) in the molecule of the initial sulphenamide occupies an axial position and is close to the α-imide group, which favours the intramolecular proton transfer and the cleavage of the ring with formation of the sulphenamide:[83]



The cleavage and elimination side reactions occur also in other cases, but the indentification of the products is difficult owing to their low stability.[82]

The sulphimides of the unsubstituted and methyl-substituted *cis*-1-thiadecalins having the α- and β-configurations proceed differently under the rearrangement conditions.

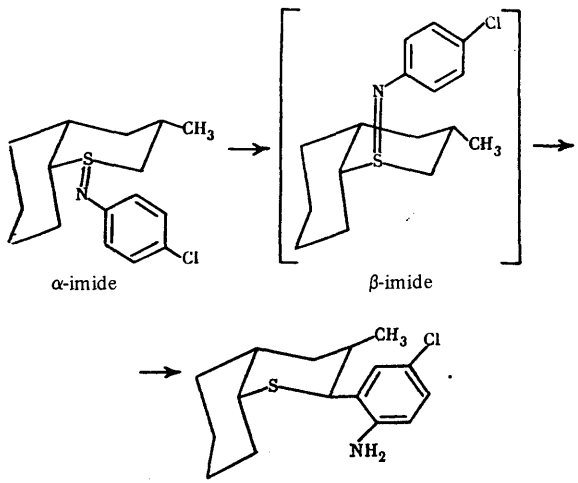


cis-1-Thiadecalin 1β-arylimide give rise to only one rearrangement product with the aryl group in the β-position, whose yield is 60%. The rearrangement of the isomeric

α-imide leads to a mixture of the α- and β-aryl-substituted products formed in proportions of 1 : 2 in an overall yield not exceeding 12%.

In the rearrangement of the α-imides, powerful *syn*-axial interactions between the aryl group and the methylene group in the 8-position must inevitably take place in the transition state, which is the cause of the formation of sulphenamides in a side reaction (the CH_2 group is in the β-position relative to the imide functional group) and of the decrease of the yield of the 2α-aryl-substituted products. The rearrangement product exists preferentially in the conformation with an equatorial aryl group at C(2).

Under the rearrangement conditions, 3α-methyl-*cis*-1-thiadecalin 1α-*N*-arylimide is converted into the 2β-aryl-substituted product, whose formation does not follow from the [2,3]-sigmatropic rearrangement of the initial sulphimide. Under the reaction conditions, the α-imide probably isomerises to the β-imide and the latter undergoes the [2,3]-sigmatropic rearrangement to the 2β-aryl-substituted product:[82]

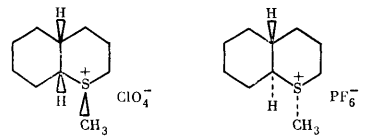


The β-sulphimides of the methyl-substituted *cis*-1-thiadecalins (the 3β-methyl-, 10-methyl-, 6α-methyl-, or 8α-methyl derivatives) give rise to 2β-aryl-substituted products on heating in triethanolamine (in 16–40% yield).

Thus the rearrangement of the *cis*- and *trans*-1-thiadecalin 1-*N*-arylimides proceeds with formation of the C(2)–aryl bond in the *cis*-position relative to the sulphimide functional group in the initial imide, i.e. suprafacially relative to the sulphimide fragment, whereupon assymetry is transferred from the sulphur atom to the C(2) carbon atom. The stereospecificity of the reaction is caused by the rigorous requirement for the retention of the orbital symmetry in the rearrangement.[82] Transfer of the aryl group to the angular position is not observed.

5. The *S*-Methylsulphonium Salts of *cis*- and *trans*-1-Thiadecalins

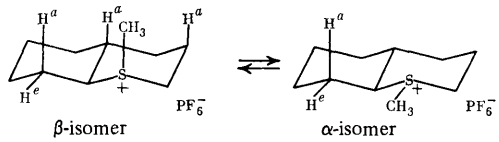
The *S*-methylsulphonium salts of *cis*- and *trans*-1-thiadecalins have been obtained by methylation with methyl iodide (with the subsequent exchange of I^- for ClO_4^-) or trimethyloxonium hexafluorophosphate.[91] 1β-Methyl-*cis*-1-thiadecalinium perchlorate constitutes a conformationally mobile system. The conformational equilibrium has been investigated by ^{13}C NMR at a low temperature in deuterioacetone (the ratio of the equatorial and axial conformers is 3 : 2).[91,92]



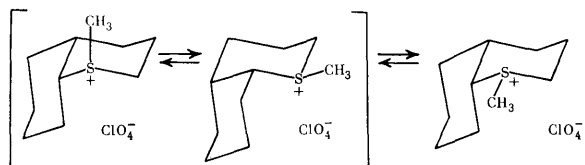
The reaction of *trans*-1-thiadecalin with trimethyloxonium hexafluorophosphate gives rise to the configurationally pure 1α-methyl isomer.[91]

The above *S*-methyl-*cis*- and *S*-methyl-*trans*-1-thiadecalinium salts undergo the pyramidal inversion at the sulphur atom on heating in deuterioacetonitrile, which makes it possible to detect diastereoisomers which are not formed on alkylation, for example, 1α-methyl-*cis*-1-thiadecalinium perchlorate or 1β-methyl-*trans*-1-thiadecalinium hexafluorophosphate.

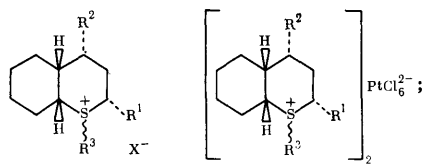
The free energy difference $-\Delta G^0_{SCH_3}$ for the two diastereoisomeric *S*-methyl derivatives of *trans*-1-thiadecalin with the equatorial and axial positions of the SCH_3 groups amounts to 0.80 ± 0.04 kcal mol^{-1}; the isomer with an axial methyl group is evidently destabilised by the *syn*-axial interaction with the hydrogen atoms at C(3), C(10), and C(8):[91,92]



The β-isomer of the *S*-methyl-*cis*-1-thiadecalinium salt exists as an equilibrium mixture of two conformers with the equatorial conformer predominating ($\Delta G^0 = -0.24$ kcal mol^{-1}). When this mixture is heated, the α-isomer is formed as a result of the inversion of the configuration at the heteroatom. The α-isomer of *S*-methyl-*cis*-1-thiadecalinium perchlorate is less favourable to the extent of 1.2 kcal mol^{-1}:[92]



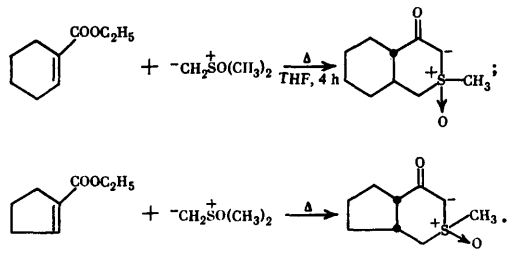
The corresponding sulphonium salts are obtained by alkylating 2α, 4α-diaryl-*cis*-1-thiadecalins with bromoacetic acid, methyl chloroacetate, acrylic acid, or methyl acrylate in the presence of hydrogen chloride.[13] The alkylation reaction usually yields a mixture of diastereoisomers with one of them predominating, but the configuration of this sulphur atom has not been determined:



$R_3 = CH_2COOH$, CH_2COOCH_3, CH_2CH_2COOH, $CH_2CH_2COOCH_3$; $X^- = Cl^-$, ClO_4^-.

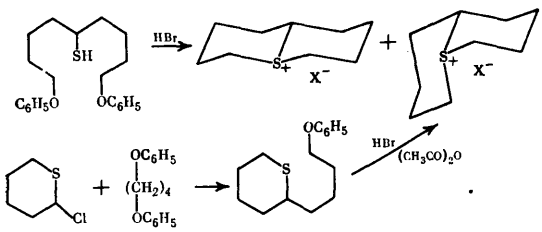
The oxosulphonium salts of condensed thiacyclohexanes are unknown. Our attempt to obtain the oxosulphonium salts by methylating 2,4-diaryl-*cis*-1-thiadecalin 1-oxides with

methyl iodide, i.e. by the method usually employed for the synthesis of acyclic oxosulphonium salts, was unsuccessful. However, oxosulphonium ylides, obtained by an indirect procedure involving the treatment of 1-ethoxycarbonylcycloalkenes with dimethylsulphoxonium methylide, have been described in the literature:[93,94]



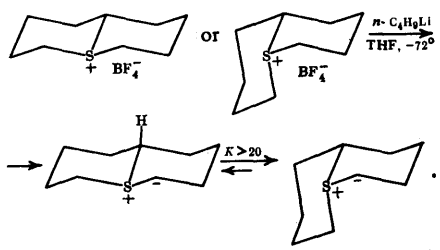
These oxosulphonium ylides are valuable intermediates in organic synthesis, for example, in the synthesis of cyclohexane derivatives with a specific configuration.[93]

The prospects for the use of sulphonium salts, and ylides based on them, as possible organic synthetic intermediates are responsible for the interest in 1-thioniabicyclo[4.4.0]-decane salts.[95-99] These are known under the name of Eastman's salts[95] and constitute a condensed heterocyclic system in the angular position of which the sulphonium centre is located. They were first obtained on heating 5-mercapto-1,9-diphenoxynonane with hydrobromic acid as a mixture of the *cis*- and *trans*-isomers in proportions of 2:3. The isomers were separated by preparative column chromatography on silica gel.[95] Eastman's salts can also be obtained from 2-chlorothiacyclohexane and phenoxybutylmagnesium chloride in the reaction involving subsequent treatment with hydrobromic acid:[96]

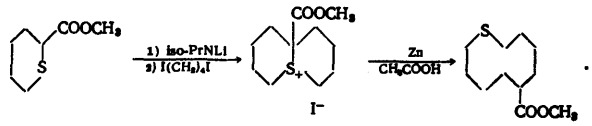


On heating to 260–270 °C in chloroform or methylene chloride, each isomer is converted into a 3:2 equilibrium mixture of the *cis*- and *trans*-isomers, formed as a result of pyramidal inversion at the sulphur atom. Heating at a lower temperature (110 °C) gives rise to a mixture in which the *trans*-isomer predominates (up to 70%).[96]

Sulphonium ylides have been obtained from *cis*- and *trans*-1-thioniabicyclo[4.4.0]decanes and their interconversion by pyramidal inversion at the sulphur atom has been investigated. It has been shown that the ylide structure in which the electron pairs of the carbanion and the heteroatom are orthogonal has the lowest energy.[97-99]



Although a more detailed consideration of these interesting compounds is not feasible within the framework of the present review, one should note that Eastman's salts and ylides based on them are important intermediates in the synthesis of macrocyclic compounds with a ring size which is not attainable by direct cyclisation, for example, of thiacyclodecane derivatives:[97]



The ylides of 1-thioniabicyclo[4.4.0]decanes are alkylated stereoselectively, which leads to the possibility of introducing new chiral centres at this stage.[97]

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Chemical Reactions of β-Aminoketones

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The advances in the field of the chemical reactions of β-aminoketones during the period 1970-1980 are described and arranged systematically. The question of the deamination and deaminomethylation of β-aminoketones is discussed; the possibility of alkylating various nucleophiles by β-aminoketones is demonstrated and the mechanism of the alkylation reaction is discussed. In addition, data are presented on the cyclisation, reduction, and photochemistry of β-aminoketones and the applications of the latter are described.
The bibliography includes 158 references.

CONTENTS

I.	Introduction	495
II.	Deamination	495
III.	Deaminomethylation	497
IV.	Alkylation by β-aminoketones	498
V.	Cyclisation	501
VI.	Reduction	505
VII.	Reactions with organometallic compounds	507
VIII.	Photochemical reactions	509
IX.	Other reactions	511

I. INTRODUCTION

The literature for 1970–1980 on the synthesis of β-aminoketones were surveyed in a previous review.[1] During the period 1960–1970, another review article was devoted to the same topic.[2] Data on the aminoacid analogues of β-aminoketones were first surveyed in another communication by the present authors.[3]

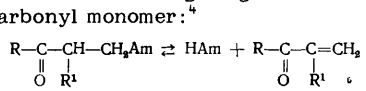
The high reactivity and also the ready availability of β-aminoketones have long attracted the attention of chemists throughout the world. Various aminoalcohols, heterocycles, αβ-unsaturated ketones, and other compounds are synthesised from them.

This paper presents a systematic account of the advances during the last decade in the field of the chemical reactions of β-aminoketones. The question of the deamination and deaminomethylation of β-aminoketones is examined. In addition, the possibility of alkylating various nucleophiles by β-aminoketones is demonstrated and the mechanism of the alkylation reaction is discussed. Data on the synthesis of secondary and tertiary γ-aminoalcohols from the corresponding β-aminoketones either by the reduction of the latter or by their interaction with organometallic compounds are surveyed. The photochemical reactions of β-aminoketones and other reactions are described.

Extensive experimental data concerning the chemical reactions of β-aminoketones have accumulated during the last decade. The β-aminoketone molecule contains two functional groups: the carbonyl and amino-groups, and the chemical reactions described below are mainly associated with these groups.

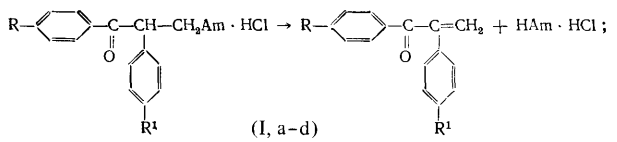
II. DEAMINATION

One of the characteristic properties of β-aminoketones is their αβ-deamination reaction, giving an amine and an unsaturated carbonyl monomer:[4]



The synthesis of carbonyl monomers from Mannich bases is based on the fact that the latter contain a mobile hydrogen atom in the α-position and tend to eliminate the amine residue. The elimination reaction has been discussed previously in a number of communications.[5-7]

The problem of the stability of β-aminoketones is particularly important for the search for new medicinal drugs. In view of this, a number of workers[8-12] investigated the kinetics of the elimination reactions of the hydrochlorides of substituted propiophenones (I, a-d) as a function of the size of the alkoxy-group, the character of the amino-group, the pH of the medium, and temperature.



(I, a-d)

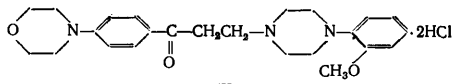
(a) Am=NC_5H_{10}, NC_4H_8, R=H, HO, CH_3O, ..., $C_7H_{15}O$, iso-C_3H_7O, iso-$C_5H_{11}O$, R^1=H;
(b) Am=NC_4H_8O, R=H, HO, CH_3O, ..., $C_5H_{11}O$, iso-$C_5H_{11}O$, R^1=H;
(c) Am=NC_4H_8, R=H, R^1=CH_3O, ..., $C_5H_{11}O$, iso-C_3H_7O, iso-C_4H_9O, iso-$C_5H_{11}O$;
(d) Am=NC_5H_{10}, NC_4H_8O, R=H, R^1=CH_3O.

On the basis of the results, Gevorgyan et al.[9] concluded that the replacement of the hydrogen atom in the *p*-position in the benzene ring by the methoxy-group, as in compound (Ia, Am = NC_4H_8; R = CH_3O; R^1 = H), reduces the rate of elimination. However, it has been noted that, on further increase in the length of the alkyl group, as in compounds (Ia, Am = NC_4H_8; R = CH_3O, ..., $C_7H_{15}O$; R^1 = H), the influence of the latter diminishes, which entails an increase of the rate of elimination. An analogous behaviour has been observed also after the introduction of the propoxy-group in the *p*-position in the benzene ring at the α-carbon atom, as in compound (Ic, R = H, R^1 = C_3H_7O).[11]

It has been established that[8,9] the rate of elimination increases with increase of temperature and the pH of the medium. The rate of elimination is appreciably influenced also by the basicity of the amino-group.[8] Thus it has been shown in relation to the hydrochlorides of β-amino-α-phenyl-4-butoxypropiophenones (I, a and b) that derivatives of

piperidine (with the basicity constant $K_b = 1.6 \times 10^{-3}$) are much more stable than those of morpholine ($K_b = 2.44 \times 10^{-6}$). The pyrrolidine derivatives occupy an intermediate position in terms of their stability ($K_b = 1.3 \times 10^{-3}$).

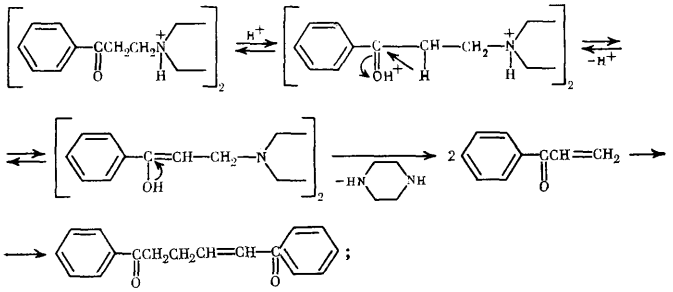
The kinetics of the elimination reaction of the dihydrochloride of 3-(4-*o*-methoxyphenyl-1-piperazinyl)-4-morpholinopropiophenone (II) have been investigated in the pH range 1–10.[13]



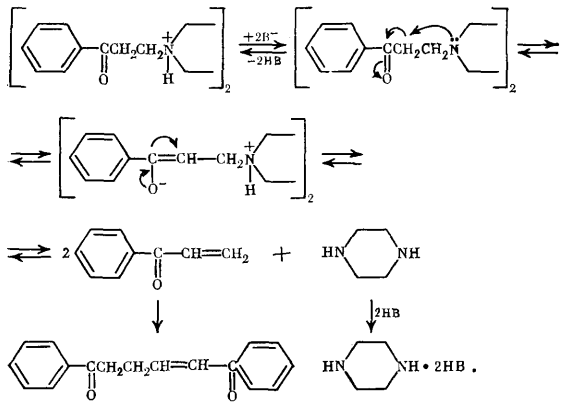
(II)

It was established that the elimination is reversible and that the degree of reaction depends on the pH. The reaction does not lead to equilibrium, since it is accompanied by a series of consecutive-parallel stages such as deaminomethylation, hydration, and dimerisation. In highly acid media the elimination reaction of the protonated form of the Mannich base (II) is an acid-catalysed process. A study has also been made[14–16] of the kinetics of the elimination reaction of the dihydrochloride of 1,4-bis(β-benzoylethyl)piperazine (III) as a function of the nature of the solvent, the pH, the ionic strength of the medium, and the buffer concentration. It has been established that compound (III) exhibits the highest stability at pH 4.5, while at pH 5.1 the main process is the elimination of the amine; at pH 6.0 a cleavage-addition process takes place. Two mechanisms have been proposed for the elimination reaction at pH < 3.5 and pH > 3.5:

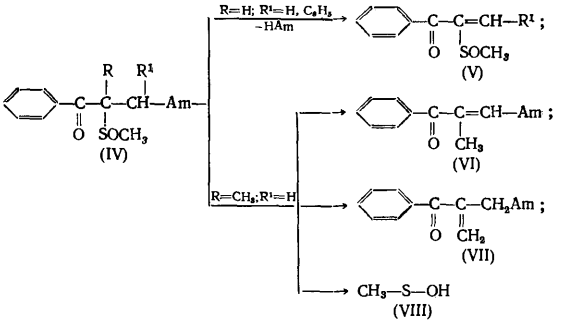
(1) at pH < 3.5:



(2) at pH > 3.5:



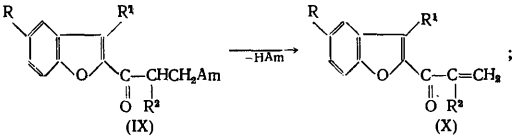
Depending on whether there are substituents in the α- and β-positions, the β-amino-α-methanesulphinylpropiophenones (IV) undergo the elimination reaction in different ways: compounds (IV) with R = R^1 = H decompose at room temperature, while those with R = H and $R^1 = C_6H_5$ distil at t = 180 °C under a pressure of 10^{-2} mmHg with formation of the vinyl ketone (V) and an amine. On the other hand, distillation of the aminoketone (IV, R = CH_3; R^1 = H) gives rise to a mixture of the products (VI), (VII), and (VIII)[17,18] whose structures have been established by physicochemical methods of analysis.



(a) R=H, CH_3; R^1=H; Am=N$(CH_3)_2$, N$(C_2H_5)_2$, NC_4H_8, NC_5H_{10}; (b) R=H; R^1=C_6H_5; Am=N$(CH_3)_2$, NC_4H_8, NC_5H_{10}.

Other studies on the synthesis of vinyl ketones from β-aminoketones have also been carried out.[19–23]

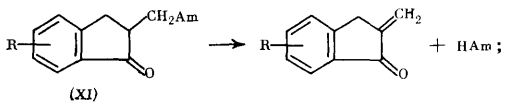
According to the data of Faure and Mattioda,[24] the deamination of 3-amino-1-(substituted 2'-benzofuryl)-1-propanones (IX) by one of four methods (pyrolysis, heating in an aqueous alkaline medium, steam distillation, and treatment of the quaternary ammonium slats in an aqueous alkaline medium) leads to the vinyl ketones (X).



R=R^1=R^2=H, Am=N$(CH_3)_2$, NC_5H_{10};
R=Cl, Br, CH_3O, R^1=R^2=H,
Am=N$(CH_3)_2$, N$(C_2H_5)_2$, NC_5H_{10};
R=H, R^1=R^2=CH_3, Am=N$(CH_3)_2$;
R=H, CH_3O, R^1=CH_3, R^2=C_2H_5, Am=N$(CH_3)_2$.

Owing to their instability, the latter can be isolated in a pure form only when there are alkyl substituents in the 3-position at the α-carbon atom relative to the carbonyl group.

The possibility of the polarographic monitoring of the decomposition reaction of the β-aminoketone has been demonstrated in relation to 2-piperidinomethyl-5-propyl- and 6-ethyl-2-morpholinomethyl-1-indanones (XI). The elimination reaction was carried out in aqueous solution at pH 7 and 37 °C.[25]

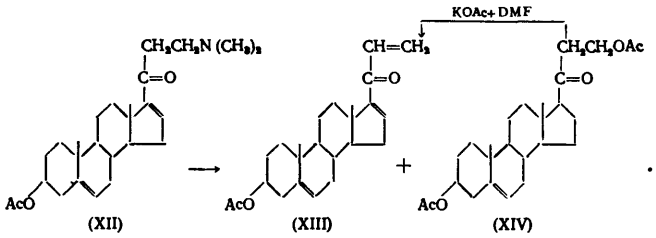


(XI)

Am=N$(CH_3)_2$, NC_4H_9, NC_5H_{10}; R=CH_3, ..., C_3H_7, iso-C_3H_7, CH_3O; Am=NC_4H_8O; R=CH_3, ..., C_3H_7, iso-C_3H_7, CH_3O, Cl, Br.

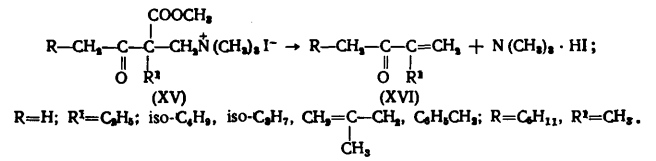
A mixture of acetic acid and acetic anhydride was used to elininate dimethylamine from 3β-hydroxy-21-dimethylaminomethylpregna-5,6-dien-20-one (XII).[26] However, the main reaction product was not the required 3-acetate of 3β-hydroxy-21-homopregna-5,16,21-trien-20-one (XIII) but

the 3,21-diacetate of 3β,21a-dihydroxy-21-homopregna-5,16-dien-20-one (XIV):

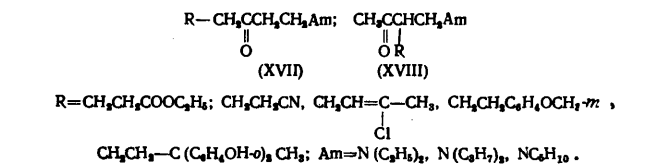


The attempts to eliminate the amine from compound (XII) by treatment with toluenesulphonic acid or phlorizil [phlorizin? (Ed. of Trans.)] were unsuccessful and led merely to an insignificant yield of compound (XIII). A solution to the problem was found by employing potassium acetate and dimethylformamide (DMF). The yield of compound (XIII) was then 65% of theoretical.

Aliphatic aminoketones also undergo the elimination reaction.[27-31] Thus a convenient method of synthesis of the vinyl ketones (XVI) in DMF at 75 °C in the course of 48 h was developed on the basis of the quaternary salts of the β-aminoketones (XV):[27]

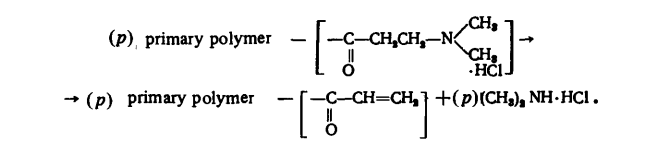


When a mixture of the isomeric aminoketones (XVII) and (XVIII) is heated at 60–120 °C, only compound (XVIII) undergoes the elimination reaction, while compound (XVII) is entirely stable under these conditions:[28]

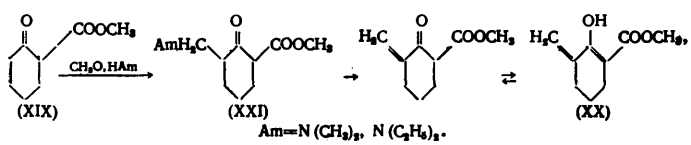


A method has been proposed for the determination of 1-diethylamino-3-butanone in the synthesis of methyl vinyl ketone.[29]

An example of the formation of a vinyl ketone also from a β-aminoketone containing a polymeric fragment has been described:[30]

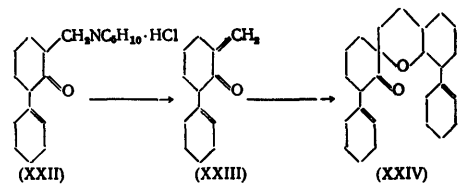


The aminomethylation of 2-methoxycarbonyl-1-cyclohexanone (XIX) by reaction with paraformaldehyde and dialkylamines in dioxan at 80 °C in the course of 8 h leads to the enolic form of 2-methoxycarbonyl-6-methylene-1-cyclohexanone (XX) with a yield of 37%:[32]



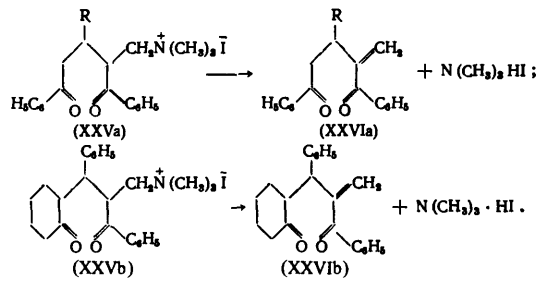
The authors explained the formation of compound (XX) by the initial appearance of 2-dialkylaminomethyl-2-methoxycarbonyl-1-cyclohexanone (XXI) followed by the elimination of the amine.

The pyrolysis of the hydrochloride of 6-cyclohex-1^1-enyl-2-piperidinomethyl-1-cyclohexanone (XXIII) at 230–250 °C for 30 min leads to a 52.6% yield of 6-cyclohex-1^1-enyl-2-methylene-1-cyclohexanone (XXIII), which subsequently dimerises to spiro-[(3-cyclohexenyl-2-oxocyclohexano)-1,2^1-(8^1-cyclohexenyl-3^1,4^1,5^1,6^1,7^1,8^1-hexahydrochroman)] (XXIV):[33]

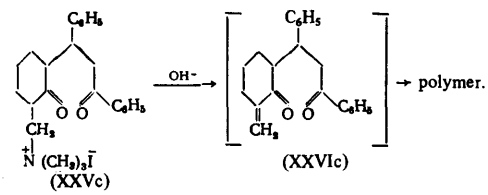


The elimination reaction involving β-aminoketones has also been described in other communications.[34-36]

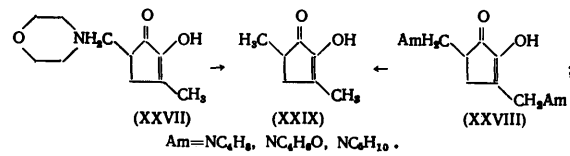
It has been shown[37-42] that the aminomethyl derivatives of diketones also tend to eliminate the amine. Thus the methiodides of dimethylaminomethyldiketones (XXV, a–c) give rise to quantitative yields of the substituted vinyldiketones (XXVI, a–c) in the presence of sodium carbonate either at room temperature or on heating (to 60–70 °C) in DMF:



In the case of the aminodiketone (XXVc) the deamination should have produced the vinyldiketone (XXVIc), but the latter readily polymerises even at room temperature to give a hardening gelatin-like product:[39]



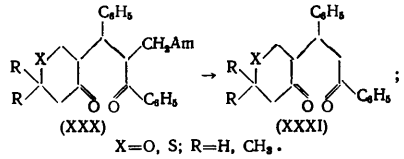
When 2-hydroxy-3-methyl-5-morpholinomethylcyclopent-2-en-1-one (XXVII) or 3,5-bisaminomethyl-2-hydroxycyclopent-2-en-1-one (XXVIII) is heated in acetic acid in the presence of zinc at 70–80 °C, 2-hydroxy-3,5-dimethylcyclopent-2-en-1-one (XXIX) is formed:[43,44]



III. DEAMINOMETHYLATION

It is of interest to note that, when the hydrochlorides of the aminomethyl derivatives of the diketone (XXX) are refluxed in water or ethanol, deaminomethylation and not

deamination is observed, i.e. the initial diketones (XXXI) are obtained in quantitative yields:[40,42]

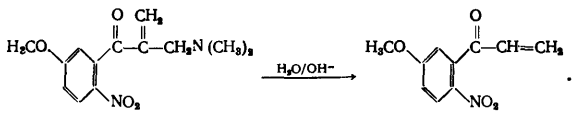


(XXX) (XXXI)

X=O, S; R=H, CH_3.

This fact accounts for the finding that the aminomethylation of the diketones (XXX) in ethanol hardly occurs.

An instance of deaminomethylation in a system where deamination is impossible for structural reasons has been described:[45]



As can be seen from the foregoing, the thermal stabilities of β-aminoketones are various: some of them undergo the elimination reaction at room temperature[17,18,36,37] but the majority undergo this reaction at an elevated temperature.[21,24,26,28,29,31,32,35-41] In a series of cases the elimination reaction is promoted by an acid medium[13-16,26] whereas in others an alkaline medium favours the reaction.[13,26,37]

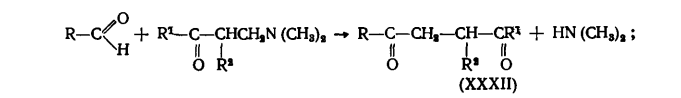
IV. ALKYLATION BY β-AMINOKETONES

Various nucleophiles ($-\rangle$ CH, $\rangle$ NH, -SH, $\rangle$ PH, -OH)

are readily alkylated by β-aminoketones. The reaction can proceed in two directions and in their treatment of the mechanism of the alkylation reaction all investigators start with the hypothesis of the initial elimination of the amine and the formation of the corresponding vinyl derivative. The subsequent interaction is regarded as one with the activated double bond formed.

(a) C-Alkylation

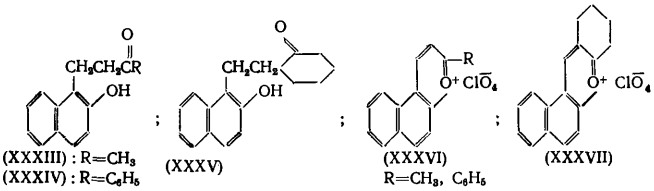
Aromatic and heterocyclic aldehydes interact with β-aminoketones in the presence of sodium cyanide or 3-ethyl-5-(2-hydroxyethyl)-4-methylthiazolidinium bromide as the catalyst with formation of the corresponding 1,4-diketones (XXXII):[46]



(XXXII)

R=CH_3, C_6H_5, 2-thienyl, 3-pyridyl, $CH_3(CH_2)_2$—, $(CH_3)_2C{=}CH$—; R^1=CH_3, C_6H_5, $(CH_3)_2C$—, —$CH{=}C(CH_3)_2$, —$C(CH_3){=}CH$—CH_3, 1-cyclopent-1-enyl, or 1-cyclohex-1-enyl; R^2=H, CH_3, C_6H_5.

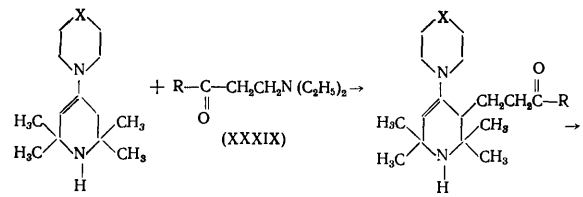
The alkylation of 2-naphthol by the β-aminoketones synthesised from acetone, acetophenone, or cyclohexanone yielded the alkyl(aryl) β-(2-hydroxy-1-naphthyl)ethyl ketones (XXXIII)–(XXXV), which were subsequently converted into the pyrylium salts (XXXVI) and (XXXVII).[47]



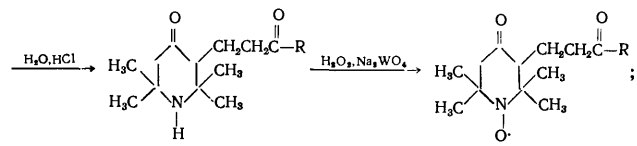
(XXXIII): R=CH_3
(XXXIV): R=C_6H_5 (XXXV) (XXXVI) (XXXVII)
R=CH_3, C_6H_5

The authors were able to alkylate only the 2-naphthol. Resorcinol does not react with β-diethylaminopropiophenone, while the interaction with 4-diethylamine-2-butanone gives rise to high-molecular-weight compounds. Phenol cannot be alkylated by β-aminoketones even in the presence of sodium hydroxide and sodium ethoxide.

Alkylation of the enamines (XXXVIII) by the β-aminoketones (XXXIX) afforded 3-(2-acylethyl-2,2,6,6-tetramethyl-4-oxopiperidines (XL), which were converted into the corresponding nitroxy-radicals (XLI) by oxidation with the H_2O_2–Na_2WO_4 mixture in accordance with the scheme[48]



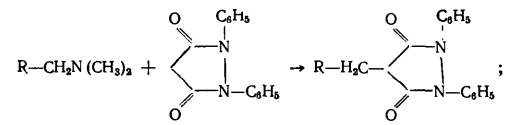
(XXXVIII) (XXXIX)



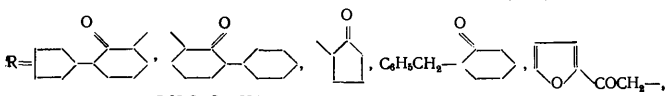
(XL) (XLI)

X=O, CH_2, R=C_6H_5, p-$CH_3OC_6H_4$, $C_6H_5CH{=}CH_2$.

New 4-substituted pyrazolidines (XLII) have been obtained by alkylating the sodium salt of 3,4-dihydroxy-1,2-diphenylpyrazolidine (XLIII) with β-aminoketones:[49]

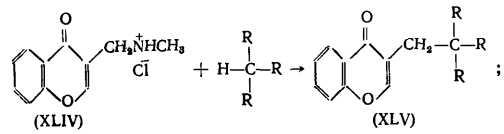


(XLIII) (XLII)

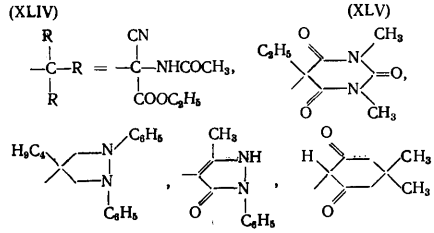


$C_2H_5OCO(CH_2)_2COCH_2$—, $HOOC(CH_2)_2COCH_2$—.

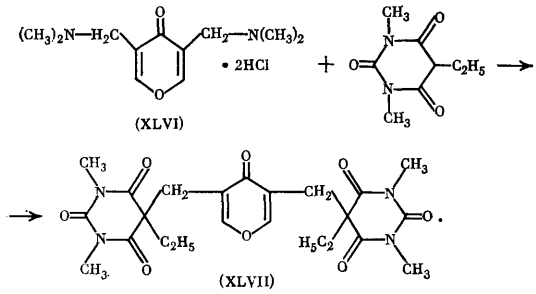
3-Substituted chromones (XLV) have been obtained by the alkylation of various CH-acid components with 3-dimethylaminomethylchromone (XLIV):[50]



(XLIV) (XLV)



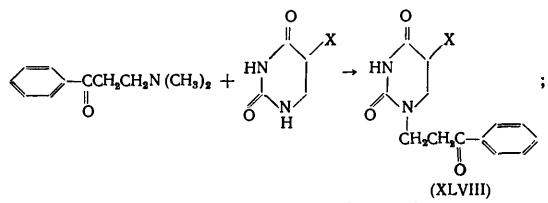
The bisaminomethyl derivatives of ketones have also been used as alkylating agents. Thus the reaction of bis-*NN'*-dimethylaminomethylpyrone (XLVI) with 5-ethyl-1,5-dimethylbarbituric acid gives rise to 3,5-bis(5-ethyl-1,3-dimethyl-2,4,6-trioxotetrahydropyrimidinomethyl)-4-pyrone (XLVII):[51]



(XLVI) (XLVII)

(b) *N*-Alkylation

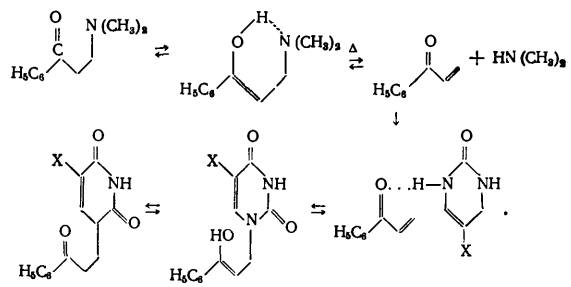
β-Aminoketones interact with 5-alkyl- and 5-halogenouracils to form the corresponding *N*-1-substituted uracils (XLVIII):[19,52]



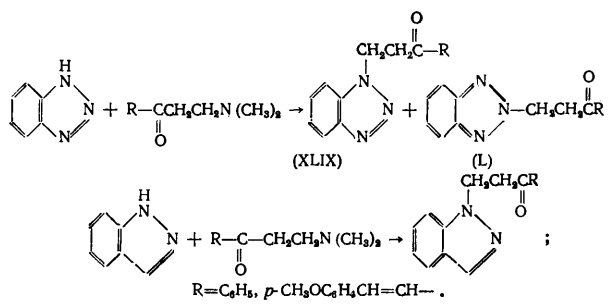
(XLVIII)

X=H, CH_3, C_2H_5, C_3H_7, Br, F.

The possible mechanisms of the alkylation of uracils have been discussed:



Tertiary β-aminoketones have been used as alkylating agents for benzotriazole and indazole:[53,54]

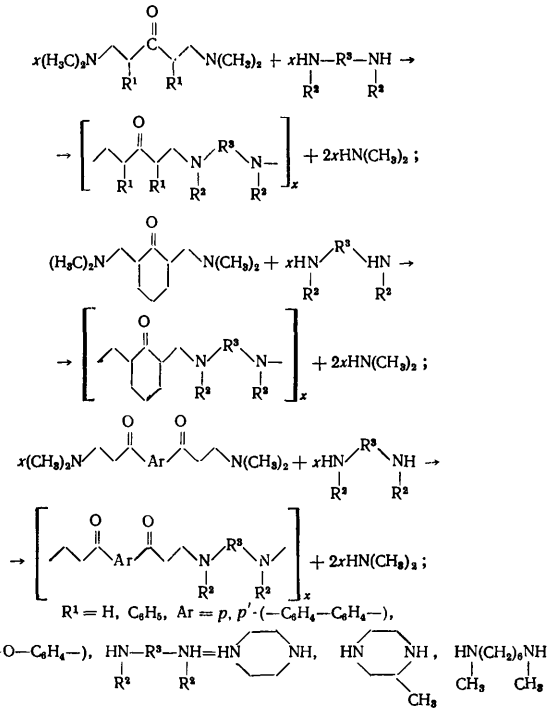


(XLIX) (L)

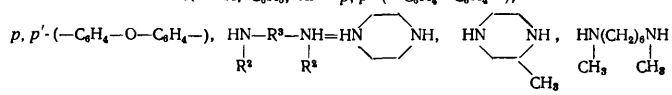
R=C_6H_5, *p*-$CH_3OC_6H_4CH{=}CH{-}$.

The alkylation of benzotriazole yields both the 1- and 2-substituted derivatives (XLIX) and (L).[53]

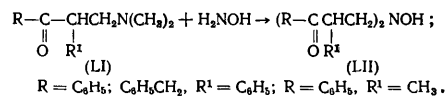
The polycondensation reaction of bisdialkylaminoketones and their methiodides with bis(secondary amines) has been described:[55,56]



R^1 = H, C_6H_5, Ar = *p*, *p'*-($-C_6H_4-C_6H_4-$), *p*, *p'*-($-C_6H_4-O-C_6H_4-$),



The stereochemistry of the resulting polymers has been investigated and a stereochemical comparison of the initial monomers has been carried out.[55,56] A number of studies have been made of the alkylation of morpholine, piperazine, dibenzylamine, and *p*-chloroaniline.[57-59] Treatment of the Mannich bases (LI) with hydroxylamine leads to the formation of compound (LII):



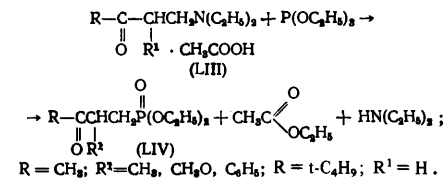
(LI) (LII)

R = C_6H_5; $C_6H_5CH_2$, R^1 = C_6H_5; R = C_6H_5, R^1 = CH_3.

When R^1 = H or CH_3 and R = CH_3, the usual oximes are formed.[60]

(c) *P*- and *As*-Alkylation

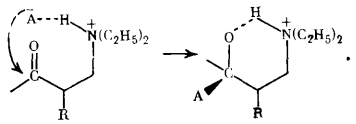
The ability of β-aminoketones to interact with nucleophiles extends also to phosphorous esters.[61,62] In their study of the kinetics of the condensation of trialkyl phosphites with the β-aminoketones (LIII), Ivanov and co-workers[63,64] concluded that a necessary condition for the interaction is the conversion of the nitrogen into the ammonium form. They selected alkyl halides, hydrochloric acid, acetic acid, water, phenol, etc. as the salt forming agents:



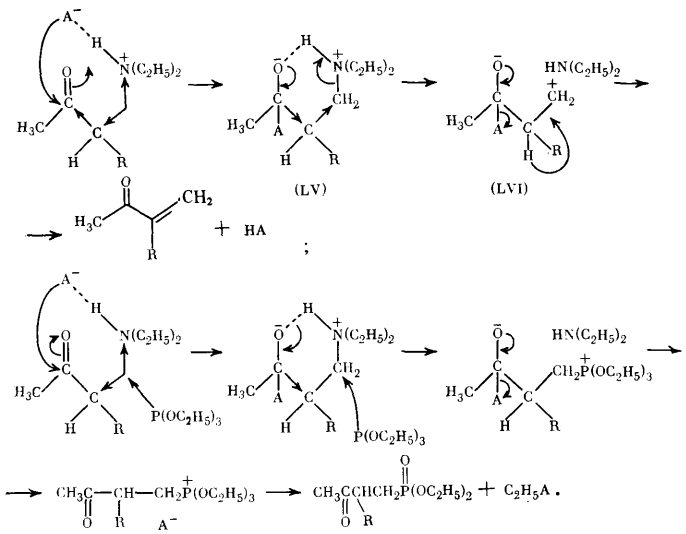
(LIII) (LIV)

R = CH_3; R^2=CH_3, CH_3O, C_6H_5; R = t-C_4H_9; R^1 = H.

As stated above, the amino-group is substituted via an elimination-addition mechanism, but the experimental data obtained in the above studies[63,64] conflict with this scheme. In all cases, on interaction with trialkyl phosphites, the β-aminoketones give rise solely to esters of ketophosphonic acids (LIV). Analysis of the results enabled the authors to conclude that the nature of the activating influence of the carbonyl group is as follows:[64]

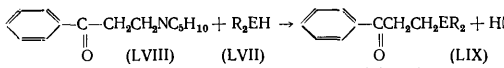


β-Aminoketones are typical ambident electrophiles and have two reaction centres with a reduced electron density: the α-carbon atom and the carbonyl carbon atom. In addition, two nucleophiles are involved in the reaction: the acid anion and triethyl phosphite. The nucleophilicity of the anion is greater than that of the phosphite and one can therefore postulate that the first reaction step is the addition of the acid anion to the carbonyl group with formation of the intermediate (LV) via the mechanism



Subsequent refinement of the reaction mechanism showed that the elimination proceeds via the intermediate (VLI) and that the stage involving the transition from compound (LV) to (LVI) should proceed at a lower rate than the stage in which compound (LV) is formed. The substitution reaction takes place via the solvation of the C(1) carbon atom by triethyl phosphite. The latter gives up its unshared electron pair in the course of the dissociation of the C–N bond to be used to form the C–P bond. The authors concluded that solvation plays a major role in accelerating the decomposition of Mannich bases.

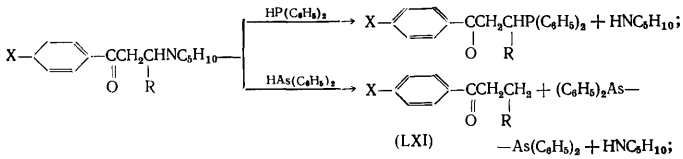
The reactions of β-aminoketones with secondary arsines and phosphines have also been investigated.[65,66] When secondary phosphines and arsines (LVII) interact with β-piperidinopropiophenone (LVIII) the corresponding phosphines and arsines (LIX) are formed smoothly in 80% yield:



E = P, As, R = C_6H_5, cyclohexyl.

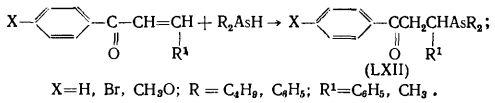
A quantitative comparison of the rates of formation of different phosphines and arsines has shown that phosphines react in ethanol faster than arsines and that the nucleophilicity of the compounds and steric factors and not the acidity of the compounds evidently play a decisive role.

The interaction of the *p*- and α-substituted β-aminoketones (LX) with diphenylphosphine and diphenylarsine leads to the formation of various products. In the latter case the hydride transfer reaction takes place, as shown by the formation of the ketone (LXI) and tetraphenyldiarsine:



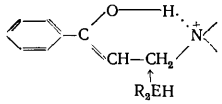
X=Br, Cl, CH_3O, R=H; X=H, R=CH_3, C_6H_5.

The ketoarsines (LXII) can be obtained by the addition of secondary arsines to unsaturated ketones:[65,66]



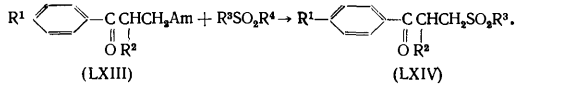
X=H, Br, CH_3O; R = C_4H_9, C_6H_5; R^1=C_6H_5, CH_3.

On this basis, the authors conclude that the alkylation evidently proceeds via a nucleophilic substitution reaction and not via vinyl ketones. They believe that a cyclic transition state of the Mannich base is formed, in which a positive charge is located at the α-carbon atom, which facilitates nucleophilic substitution.



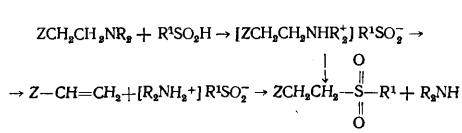
(d) *S*-Alkylation

The β-aminoketones (LXIII) react with sulphinic acids or their sodium salts to form the sulphoketones (LXIV)[67–72] (Table 1):

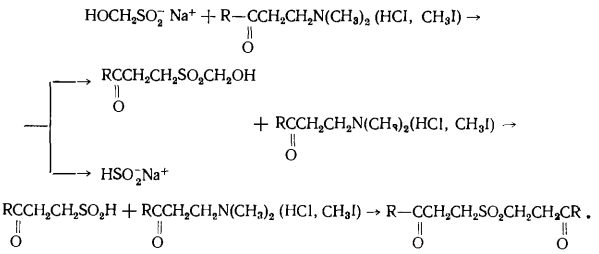


(LXIII) (LXIV)

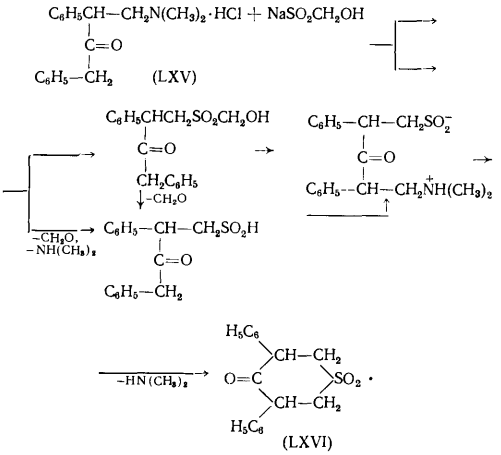
It is believed[67] that the reaction mechanism is as follows:



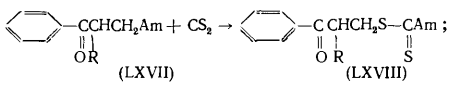
Symmetrical dialkyl sulphones have been obtained in accordance with the following scheme:[68]



The β-aminoketone (LXV) has been converted into 3,5-diphenyltetrahydrothiopyran-4-one 1,1-dioxide (LXVI):[70]

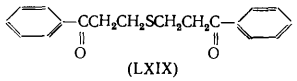


The reaction of the β-aminoketones (LXVII) with carbon disulphide leads to the formation of the substituted dithiourethanes (LXVIII):[73]



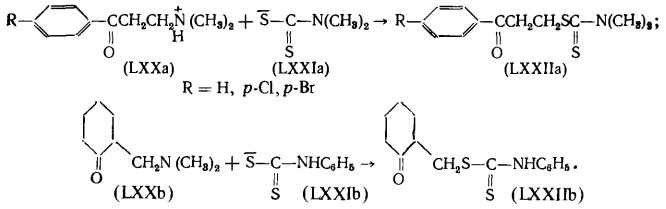
R=H, C_6H_5; Am=NC_4H_8O, NC_6H_{10}.

The same β-aminopropiophenones react with carbon disulphide in aqueous ammonia to form di(2-benzoylethyl) sulphide (LXIX):[74]



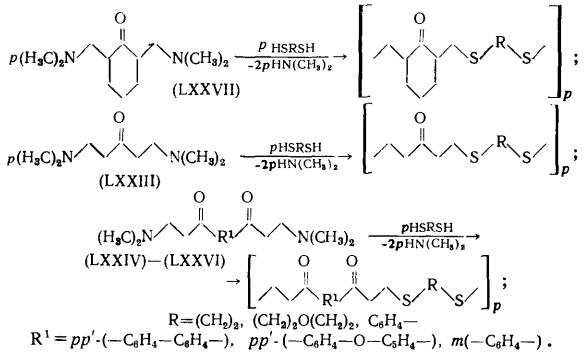
(LXIX)

The interaction of the Mannich bases (LXX, a and b) with the dithiocarbamates (LXXI, a and b) results in the elimination of the amine from the aminoketone molecule and the formation of *S*-(2-acetyl)dithiocarbamates (LXXIII, a and b):[74]



R = H, *p*-Cl, *p*-Br

The bis-Mannich bases (LXXIII)–(LXXVII), obtained from acetone, 4,4-diacetylbiphenyl, di(4-acetylphenyl) ether, 1,3-diacetylbenzene, and cyclohexanone, have been introduced into the polycondensation reaction with ethane-1,2-dithiol, oxydiethanedithiol, and 1,3-dimercaptobenzene. The reaction products are the corresponding poly(β-ketothioethers) (LXXVIII, a–d):[75,76]

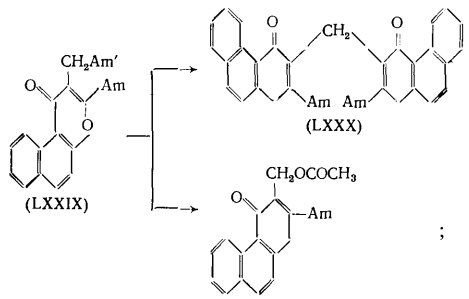


R=$(CH_2)_2$, $(CH_2)_2O(CH_2)_2$, C_6H_4—

R^1 = *pp'*-(—C_6H_4—C_6H_4—), *pp'*-(—C_6H_4—O—C_6H_4—), *m*-(C_6H_4).

(e) *O*-Alkylation

On heating in acetic anhydride at 95°–100 °C for 3–6 h, 3-dialkylamino-2-dialkylaminomethyl-1-oxo-1*H*-naphtho[2,1-*c*]pyrans (LXXIX) are converted into 2,2'-methylenebis{3-dialkylamino-1-oxo-1*H*-naphtho[2,1-*c*]pyrans} (LXXX) in satisfactory yields:[77]



(LXXIX) (LXXX) (LXXXI)

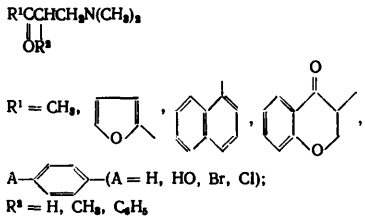
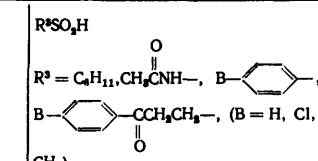
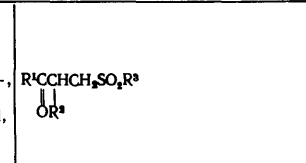
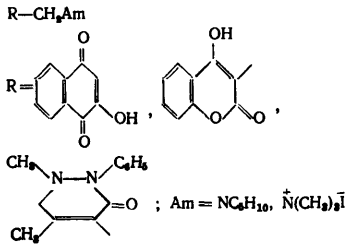
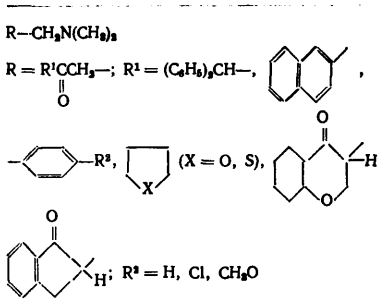
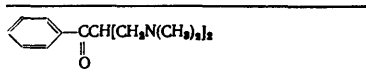
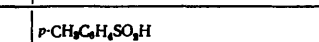
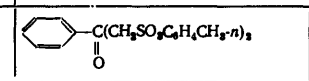
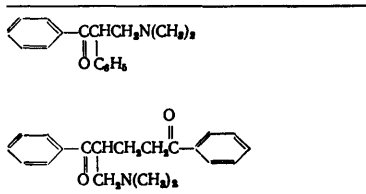
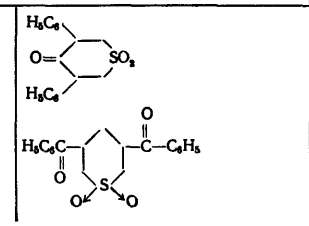
Am=$N(CH_3)_2$, $N(C_2H_5)_2$, NC_4H_8, NC_5H_{10}, $N(CH_3)(CH_2C_6H_5)$, $N(iso\text{-}C_3H_7)_2$, $N(CH_2—CH=CH_2)_2$; Am'=NC_4H_8O, NC_5H_{10}.

When Am = Am' = NC_5H_{10}, the *O*-alkylation product, namely 2-acetoxymethyl-1-oxo-3-(*N*-piperidyl)-1*H*-naphtho[1,2-*c*]pyran (LXXXI), is obtained in 34% yield together with compound (LXXX).

V. CYCLISATION

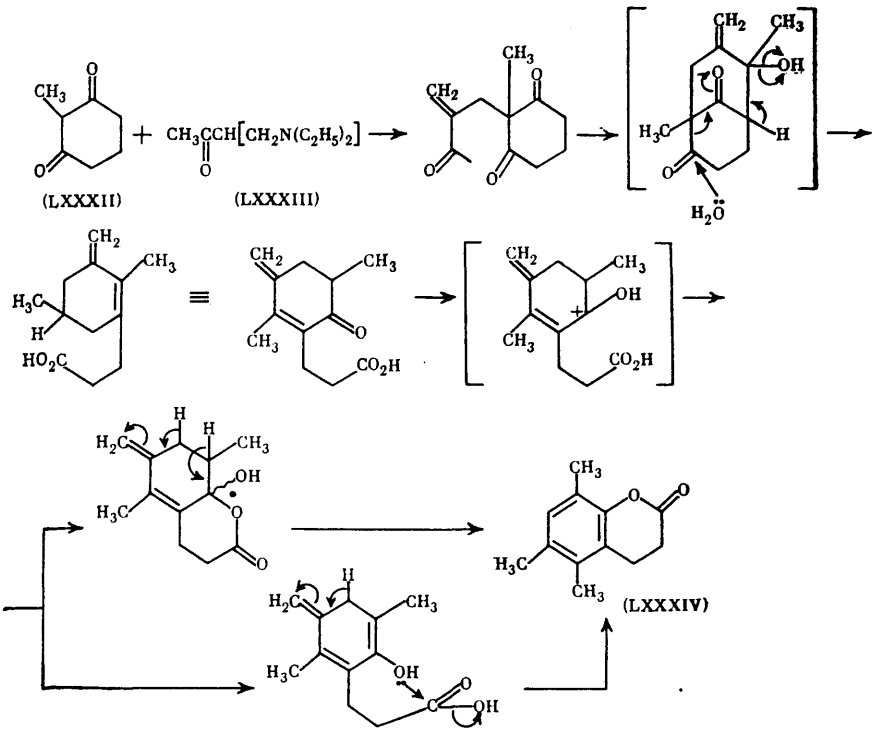
It is known that Mannich bases (β-aminoketones) can serve as intermediates in the synthesis of various heterocyclic compounds via cyclisation reactions. The latter can be

Table 1. *S*-Alkylation.

Alkylating compound (Mannich base)	Alkylated compound	Reaction product	Yield, %	Refs.
			16—83	[67, 71, 72]
			57—79	[67]
			19—57	[69]
			53.0	[68]
			14.0 32.0	[70]

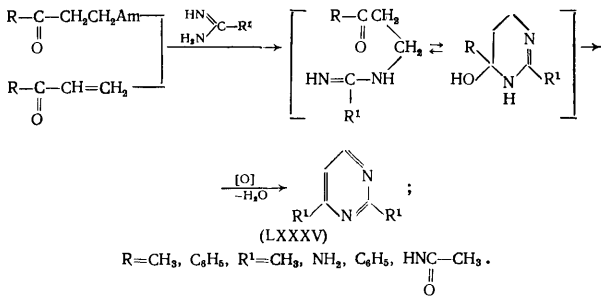
divided into two types: (1) reactions occurring with elimination of the amino-group; (2) reactions occurring without the elimination of the amino-group.

In most cases cyclisation with participation of β-amino-ketones is of the first type. In particular, when equimolar amounts of 2-methylcyclohexane-1,3-dione (LXXXII), *N*-bis-diethylaminomethylacetone (LXXXIII), and pyridine are refluxed in benzene, the dihydrocoumarin (LXXXIV) is obtained in 60% yield.[78] The ethyl analogue of compound (LXXXII) reacts analogously to the latter:



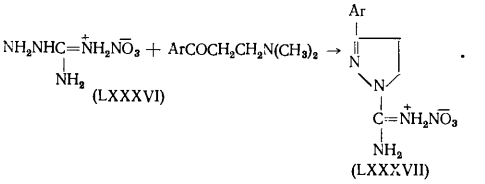
It is of interest to note that a bicyclic ketone is formed under the same conditions from 2-methylcyclopentane-1,3-dione, but its structure has not been stated.[78]

The interaction of the keto-derivatives of Mannich bases with amidines and guanidine leads to the pyrimidines (LXXXV).[79] The yield of the latter is then significantly higher than in the analogous condensation using the corresponding vinyl ketones:



The quaternary slats of β-aminoketones have also been used in this reaction, but this does not increase the yield of the corresponding pyrimidines.

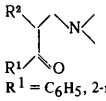
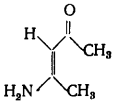
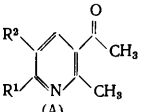
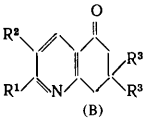
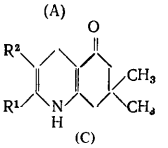
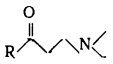
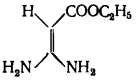
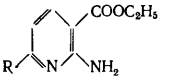
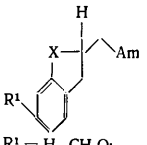
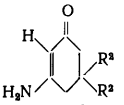
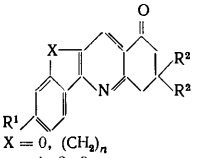
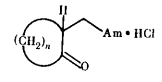
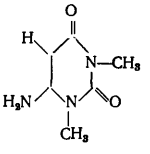
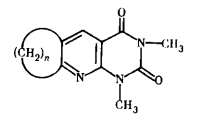
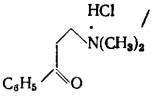
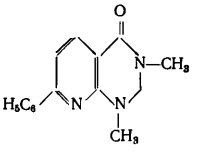
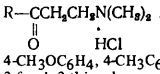
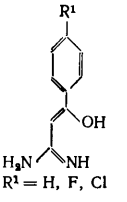
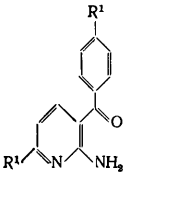
Aminoguanidinium nitrate (LXXXVI) reacts with arylaminoketones in alcoholic solutions at pH 10 to form 1-amidino-Δ^2-pyrazolines (LXXXVII):[80]



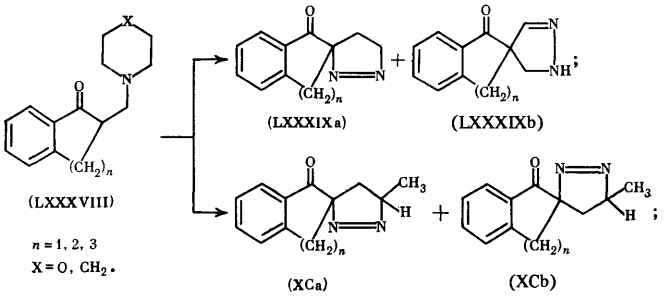
The mechanism of the formation of the pyrazoline (LXXXVII) proposed by the authors includes the conversion of the aminoketone into the vinyl ketone and its subsequent conversion into a hydrazone, which cyclises to the pyrazoline. The authors demonstrated that, depending on the pH of the medium, the reaction products can also be di-β-ketohydrazines and the dinitrates of amidinohydrazones.

2-(*N*-Aminomethyl)cycloalkanones (LXXXVIII) have been converted into the diastereoisomeric spiro-pyrazolines (LXXXIX, a and b) and (XC, a and b) with the aid of an ethereal solution of diazomethane or diazoethane.[81] The

Table 2. The synthesis of heterocycles from β-aminoketones.

Initial compound		Reaction product	Yield, %	Refs.
 $R^1 = C_6H_5$, 2-naphthyl, $R^2 = H, CH_3, C_6H_5$		 (A)  (B) $R^3 = H, CH_3$  (C)	42—57 (A), 21—54 (B), 43—62 (C)	[83]
 $R = CH_3, C_6H_5, 4\text{-}ClC_6H_4, 4\text{-}CH_3OC_6H_4$, 2-furyl, 2-thienyl			43—56	[85]
 $R^1 = H, CH_3O$; $Am = N(CH_3)_2, NC_5H_{10}$	 $R^2 = H, CH_2$	 $X = O, (CH_2)_n$ $n = 1, 2, 3$	29—47	[84]
 $Am = N(CH_3)_2, NC_5H_{10}$			32—53	[86]
	ditto		36—57	[87]
 4-$CH_3OC_6H_4$, 4-$CH_3C_6H_4$, 2-naphthyl, 2-furyl, 2-thienyl	 $R^1 = H, F, Cl$		23—69	[88]

authors proposed a probable reaction mechanism:



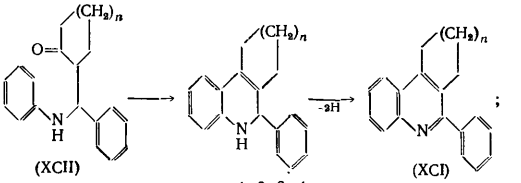
(LXXXVIII)

$n = 1, 2, 3$
$X = O, CH_2$.

(LXXXIXa) (LXXXIXb)

(XCa) (XCb)

Substituted quinolines (XCI) have been obtained by the cyclisation of 2-(1-anilinomethyl-1-phenyl)cycloalkanones (XCII) by refluxing the latter with a 9 : 1 mixture of acetic and sulphuric acids:[82]

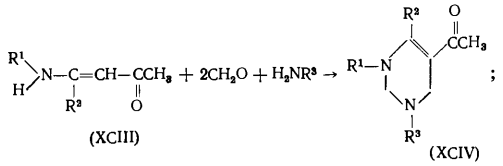


(XCII) (XCI)

$n = 1, 2, 3, 4$.

The synthesis of certain heterocyclic systems from various β-aminoketones has been described[83–88] (Table 2).

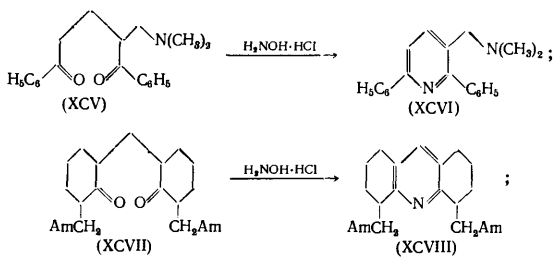
Under the conditions of the Mannich reaction with one mole of a primary amine and two moles of formaldehyde, the enaminoketones (XCIII) cyclise to the tetrahydropyrimidino-derivatives (XCIV):[89,90]



(XCIII) (XCIV)

R^1=CH_3, C_6H_5, $CH_2C_6H_5$, R^2 = H, CH_3, R^3=CH_3, $C(CH_3)_3$.

The interactions of β-aminoketones with hydroxylamine hydrochloride, formaldehyde, and other compounds are reactions of the second type.[91-95] Thus 1,3-dibenzoyl-3-dimethylaminomethylpropane (XCV) has been converted into 3-dimethylaminomethyl-2,6-diphenylpyridine (XCVI) with the aid of hydroxylamine hydrochloride, while bis(3-diamino-methyl-2-oxo-1-cyclohexyl)methane (XCVII) has been converted into 4,5-bis(aminomethyl)-*sym*-octahydroacridine (XCVIII):[91-93]

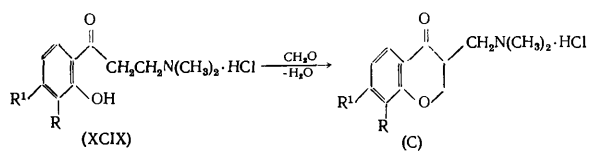


(XCV) (XCVI)

(XCVII) (XCVIII)

Am=$N(CH_3)_2$, $N(C_2H_5)_2$.

Substituted chromanones (C) have been obtained by cyclising the β-aminoketones (XCIX) with formaldehyde:[94]

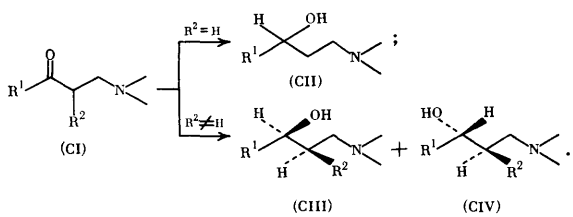


(XCIX) (C)

R, R^1 = H, CH_3O,

VI. REDUCTION

The carbonyl group of β-aminoketones can be readily converted into the hydroxy-group by reducing agents such as complex metal hydrides (lithium tetrahydroaluminate and sodium tetrahydroborate)[53,54,96-117] (Table 3), sodium amalgam,[118] and others.[106-111,119] The reduction products (γ-aminoalcohols) are of interest as biologically active substances:[97,100-102,120]

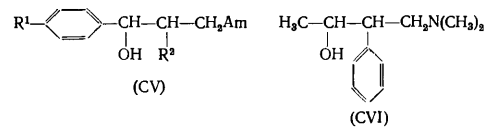


(CI) (CII) (CIII) (CIV)

It can be seen from the above scheme that the reduction of the aminoketones (CI, R^2 = H) leads to the formation of only one aminoalcohol (CII),† while the reduction of the aminoketones (CII, $R^2 \neq$ H) having an α-asymmetric centre gives rise to two diastereoisomeric aminoalcohols (CIII) and CIV).#

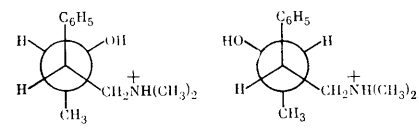
The absolute and relative configurations as well as the predominant conformations of the diastereoisomeric aminoalcohols have been determined by infrared and NMR spectroscopy and by mass-spectrometry.[98,100,105-114]

The aminoalcohols (CV) and (CVI) have been resolved into the diastereoisomers by fractional crystallisation.[98,100,112]



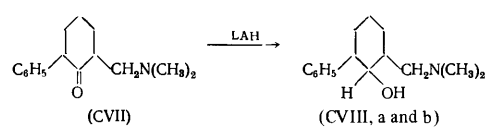
(CV) (CVI)

It has been shown[98] that the conformers (CVIa) and (CVIb) of compound (CVI) predominate.



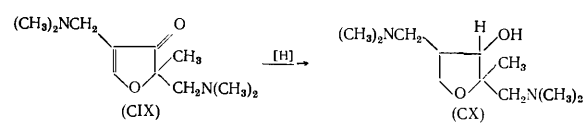
(CVIa) (*threo*) (CVIb) (*erythro*)

The reduction of the β-aminoketone (CVII), which is a derivative of phenylcyclohexanone, leads to a mixture of the stereoisomeric aminoalcohols (CVIIIa) and (CVIIIb), which has been resolved[114] into its components on a chromatographic column to give (CVIa) : (CVIb) = 3 : 1:



(CVII) (CVIII, a and b)

Whereas the reduction of 2,4-bisdimethylaminomethyl-2-methylfuran-3(2*H*)-one (CIX) with the aid of palladium on charcoal involves only the double bond, when rhodium on charcoal or sodium tetrahydroborate is used, the aminoalcohol (CX) is formed:[119]

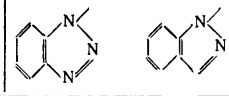
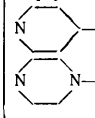
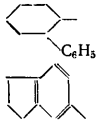
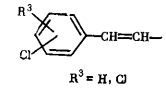


(CIX) (CX)

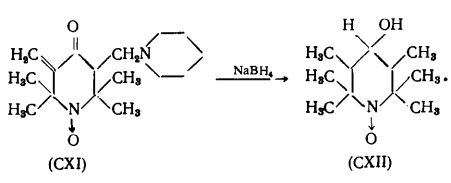
†A case is known in which achiral β-dialkylaminopropiophenones were reduced to the optically active aminoalcohols by treatment with lithium tetrahydroaluminate/(−)-menthol.[121]

#The stereochemistry of the reduction of the β-asymmetric β-aminoketones has been described.[122,123] In particular, the reaction between lithium tetrahydroaluminate and a series of β-asymmetric β-aminoketones has been investigated.[123] It has been shown that the stereoselectivity of the reduction of *NN*-dialkylamino-derivatives is greater than that of the reduction of *N*-monoalkylamino-derivatives.

Table 3. Products of the reduction of β-aminoketones.

R^1	R^2	Am	Reducing agent	Yield, %	Biological activity	Refs.
		$p\text{-}R^1\text{—}C_6H_4CH(OH)\text{—}CH(R^2)\text{—}CH_2Am$				
H, F, CH_3	n-C_3H_7 n-C_4H_9	NC_4H_8O, NC_6H_{10}, NC_6H_{12}, 	LAH $NaBH_4$	52—77	spasmolytic, neurotropic, analgesic	[100, 102]
H, CH_3O— —CH=CH—	H		$NaBH_4$	80—98	—	[53, 54]
$C_6H_5CH_2O$	CH_3		ditto	58	anticough, analgesic	[101]
F, CH_3, iso-C_3H_7, CH_3O, C_2H_5O, 2,4-$(CH_3)_2$, CH_3SO_2, 3,4-$(CH_3O)_2$, CH_3SO	H, CH_3	$N(CH_3)_2$, $N(C_2H_5)_2$, NC_4H_8, NC_5H_{10}, NC_4H_8O, NC_6H_{12}, 	LAH, $NaBH_4$	71—95	bacteriacidal, fungicidal	[96, 104]
 A = H, CH_3O, Cl OH, NO_2	H, CH_3 C_6H_5	$N(CH_3)_2$, $N(C_2H_5)_2$, NC_5H_{10}, NC_4H_8O $N(CH_3)CH_2C_6H_5$	LAH	71—93	analgesic	[112]
		$R^1\text{—}CH(OH)\text{—}CH(R^2)\text{—}CH_2Am$				
	CH_3		$NaBH_4$	50	anticough, analgesic	[101]
CH_3	C_6H_5	$(NCH_3)_2$	LAH			[98]
$(C_6H_5)_2C\text{—}R^3$ R^3 = H, OH, CH_3O	CH_3	$HNCH_3$, HNC_2H_5, $N(CH_3)_2$, NC_6H_{10}	LAH $NaBH_4$	30—78	anticonvulsant, effect on CNS	[97]
 C_6H_5, $C_6H_5CH_2CH_2$,	H	$N(CH_3)_2$, NC_6H_{10}, HN— ; $R^3 = CH_3$, $CH_2C_6H_5$, CH_2CH_2OH, A = H, CH_3, F, Cl, CH_3O	LAH $NaBH_4$	32—99	sedative	[103, 117]
 R^3 = H, Cl	$(CH_2)_4CH_3$	$N(CH_3)_2$	$NaBH_4$	32—38	—	[105]

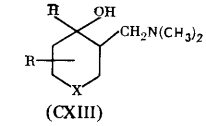
The αβ-unsaturated ketone (CXI) has been reduced to the 2,2,3,5,6,6-hexamethyl-4-hydroxypiperidin-1-yloxy-radical (CXII) with sodium tetrahydroborate:[124]



(CXI) (CXII)

Deamination takes place simultaneously.

A number of studies have been devoted to the stereochemical characteristics of the reduction of the aminomethyl derivatives of tetrahydropyran-4-ones and tetrahydrothiopyran-4-ones to the aminoalcohols (CXIII).[106-111]

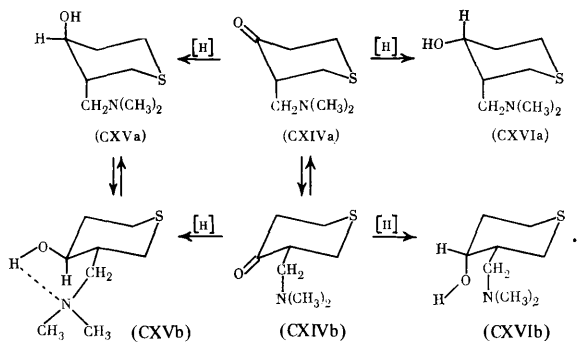


(CXIII)

R = CH_3, $(CH_3)_2$, $(CH_3)_3$, $CH_2N(CH_3)_2$, X = O, S.

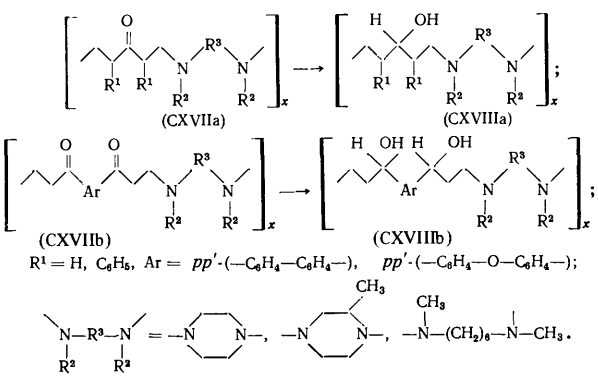
The quantitative ratios, the steric configurations, and the predominant conformations of the stereoisomeric aminoalcohols have been established by gas-liquid chromatography (GLC) and infrared and ^1H NMR spectroscopy and the steric specificity of the test reactions has been elucidated. It has been shown in a number of instances[107,110,111] that the quantitative ratio of the stereoisomeric aminoalcohols depends on the character of the reducing agent and the reaction conditions.

It has been noted that the equatorial isomers of the corresponding alcohols predominate in the reduction of the unhindered and conformationally stable 4-oxotetrahydro-1-thiopyrans (CXIV) with lithium tetrahydroaluminate, while in the reduction with aluminium isopropoxide the axial isomers are the dominant ones,[107] which agrees with the available data.[125] The individual isomers (CXV) and (CXVI) have been isolated by crystallising the mixture:



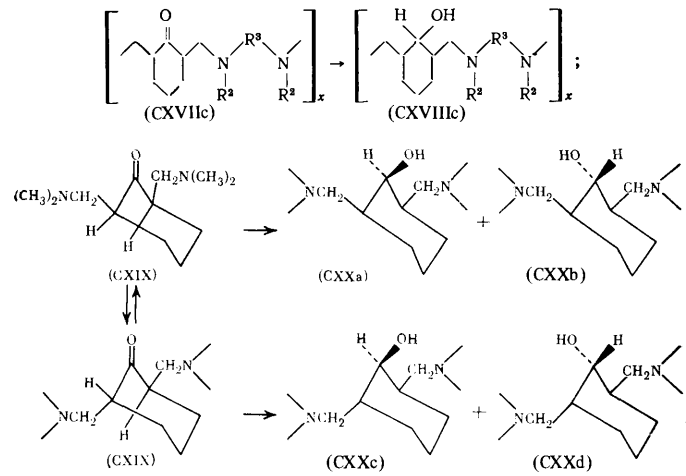
The authors[107] concluded that the aminoketone (CXIV) is reduced preferentially in the conformation (CXIVb), which should be promoted by the formation of a cyclic complex of the chelate type with participation of the metal hydride and the carbonyl amino-groups.[125] The reduction with participation of the conformation (CXIVa) followed by the conversion of the aminoalcohol conformers (CXVa) and (CXVIa) formed initially into compounds (CXVb) and (CXVIb) respectively is less likely, since this involves breaking the stereochemical rules governing the reduction of six-membered cyclic ketones.[126]

Data concerning the reduction of poly-β-dialkylaminoketones (CXVII) to the corresponding poly-γ-aminoalcohols (CXVIII) have been published:[127]



$R^1 = H, C_6H_5$, Ar = *pp'*-(—C_6H_4—C_6H_4—), *pp'*-(—C_6H_4—O—C_6H_4—);

For comparison, a study has also been made of the reduction of the corresponding monomeric aminoketones. The stereochemistry of the reduction products (both polymeric and monomeric) has been investigated. The reduction has been carried out both with lithium tetrahydroaluminate and catalytically:[127]



The reduction of the bis-Mannich base (CXIX) with lithium tetrahydroaluminate leads to the formation of all the possible stereoisomeric aminoalcohols (CXX, a–d). It has been established[127] that fragments having three configurations alternate in the polymeric γ-aminoalcohols:

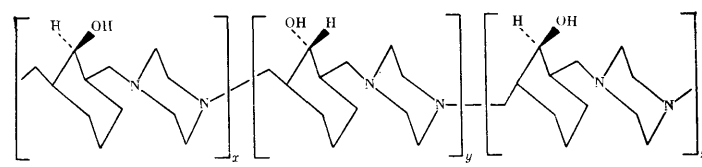
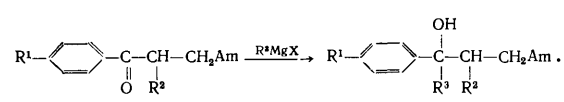


Table 4. Products of the interaction of β-aminoketones with a Grignard reagent.

R^1	R^2	R^3	Am	Biological activity	Refs.
H, CH_3, F	CH_3, C_2H_5, $C_6H_5CH_2$, C_6H_{11}	CH_3, C_2H_5, n-C_3H_7	$N(CH_3)_2$, NC_6H_{12}, N⟨⟩N—CH_3	—	[100, 102]
H	C_2H_5	H	NC_5H_{10}, NC_4H_8O	—	[99]
C_6H_5	C_2H_5, C_3H_7	H	NC_5H_{10}	morphine-like	[112]
CH_3, CH_3O, iso-C_3H_7	$C_6H_5CH_2$	H	$N(CH_3)_2$, $N(C_2H_5)_2$, NC_4H_8, NC_4H_8O, NC_5H_{10}	bacteri-cidal	[104]

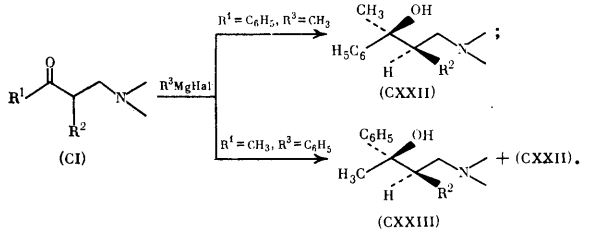
VII. REACTIONS WITH ORGANOMETALLIC COMPOUNDS

The tertiary γ-aminoalcohols (CXXI) have been obtained by the reaction of the β-aminoketones (CI) with a Grignard reagent or organolithium compounds[99–104,108,109,112,128–130] (Table 4):



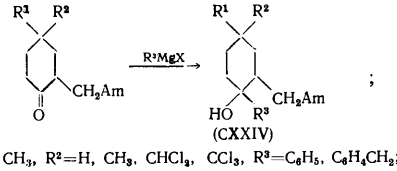
The stereochemistry of the reactions of aryl and methyl 2-aminoalkyl ketones substituted in the α-position, with Grignard reagents has been studied in detail.§ The configurations and the ratios of the diastereoisomers have been determined.[131,132]

The reaction with the phenyl-substituted aminoketones (CI, $R^1 = C_6H_5$) is 100% stereospecific and leads to the amino-alcohol (CXXII), while the reaction of the methyl-substituted ketobases (CI, $R^1 = CH_3$) takes place with the preferential formation of the diastereoisomer (CXXIII) (the optical yields are 86–100%).[133]



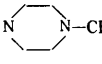
(CI) (CXXII) (CXXIII)

A large series of 4-substituted 2-aminomethyl-1-phenyl-(benzyl)cyclohexanols (CXXIV) have been synthesised by the interaction of cyclic Mannich bases with a Grignard reagent;[129] depending on the structure of the reactants, the yields are 30–80%. In particular, a relation is observed between the yields and the character of the amino-group: the best results have been obtained for the pyrrolidino- and morpholino-derivatives:

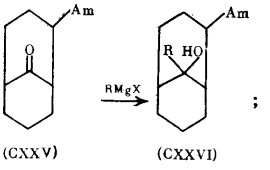


(CXXIV)

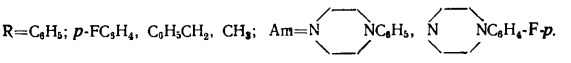
R^1=H, CH_3, R^2=H, CH_3, $CHCl_2$, CCl_3, R^3=C_6H_5, $C_6H_4CH_2$;

Am=NC_4H_8, NC_4H_8O, NC_6H_{10},  .

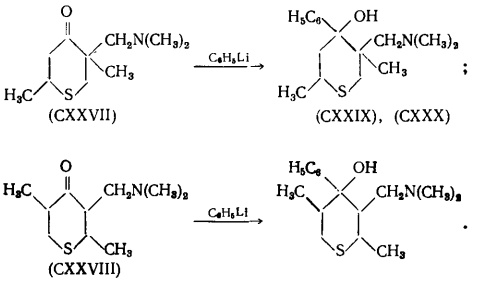
The reactions of the bicyclic Mannich bases (CXXV) with a Grignard reagent lead to the formation of the aminoalcohol (CXXVI); for R = C_6H_5, only one isomer of the aminoalcohol was isolated and its configuration established:[128]



(CXXV) (CXXVI)

R=C_6H_5; *p*-FC_6H_4, $C_6H_5CH_2$, CH_3; Am= 

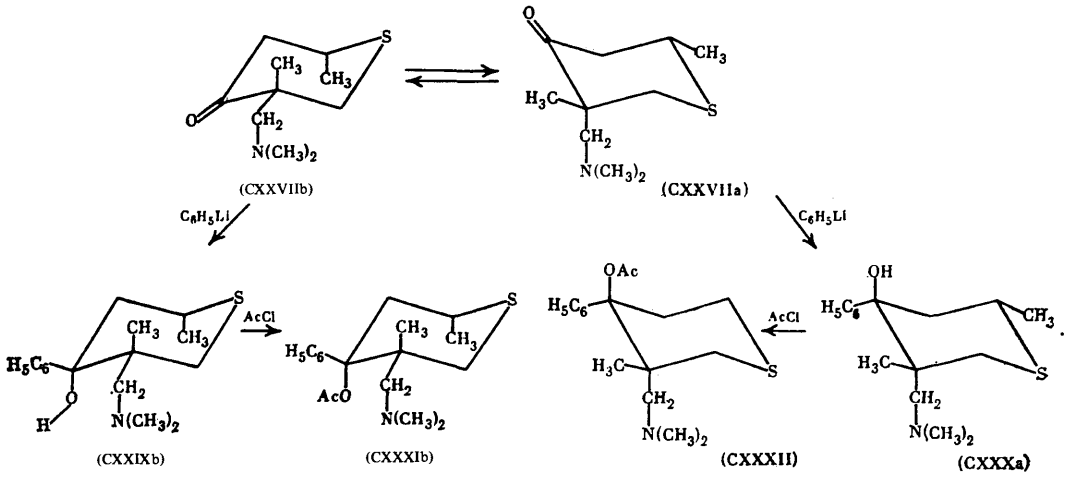
A strong predominance of one of two conformers has been observed in the synthesis of tertiary aminoalcohols from the aminomethyl derivatives of γ-ketones, in particular compounds (CXXVII) and (CXXVIII):[108,109,111,130]



(CXXVII) (CXXIX), (CXXX)

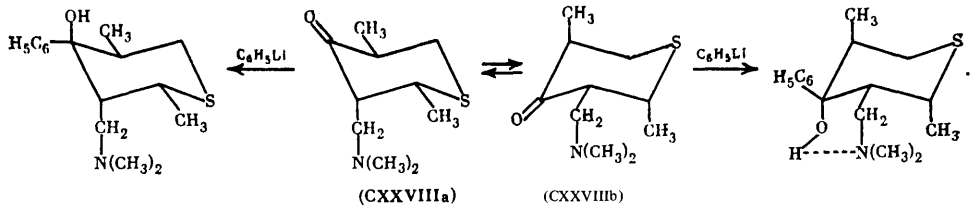
(CXXVIII)

The aminoalcohols (CXXIX) and (CXXX), which are formed as the dominant components from the aminoketone (CXXVII), have respectively the *cis*- and *trans*-configurations relative to the hydroxy- and aminomethyl group, but in solutions the conformational equilibrium is displaced towards the conformers (CXXIXb) and (CXXXa):



(CXXVIIb) (CXXVIIa) (CXXIXb) (CXXXIb) (CXXXII) (CXXXa)

§ The interaction of a Grignard reagent with β-aminoketones having an asymmetric carbon atom in the β-position or in the alkylamino-group also proceeds with a high degree of stereospecificity.[122,133,134]

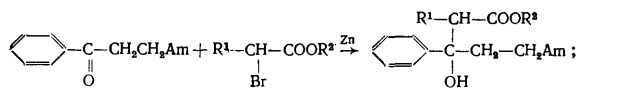


(CXXVIIIa) (CXXVIIIb)

The steric orientation of the hydroxy-groups of the amino-alcohols (CXXIX) and (CXXX) has also been confirmed by the character of the bands of the acetoxy-groups in the infrared spectra of solutions of the corresponding acetates (CXXXI) and (CXXXII).

The authors[109] concluded that the aminoketones (CXXVII) and (CXXVIII) interact with phenyl-lithium in the form of the conformers (CXXVIIb) and (CXXVIIIb) via a cyclic chelate complex with subsequent attack on the carbonyl group by the organometallic compound from the equatorial region leading to the *cis*-alcohols (CXXIXb) and (CXXXb), as shown above.

A number of studies[135-138] have been devoted to the reaction of β-aminopropiophenones (CXXXIII) with Reformatskii's reagent:



(CXXXIII)

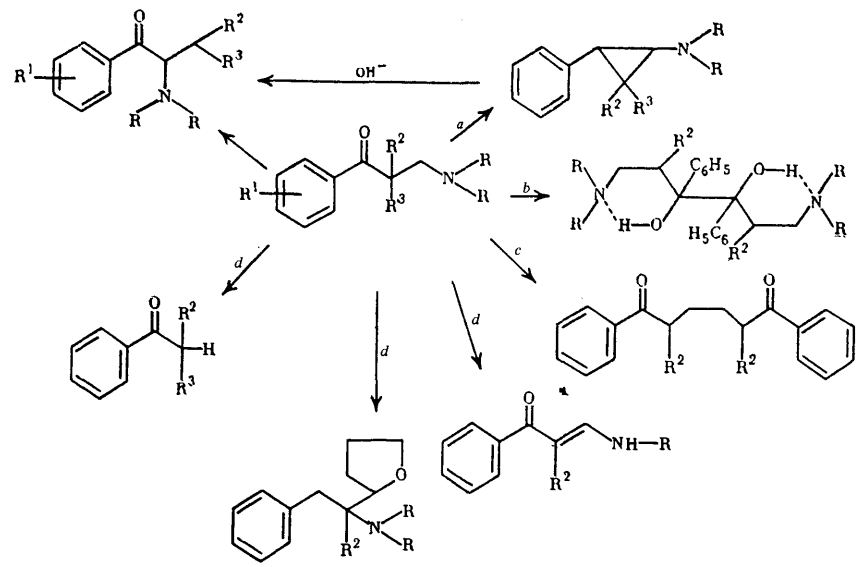
R^1=CH_3, C_2H_5, iso-C_3H_7, t-C_4H_9, R^2=CH_3, C_2H_5, Am=$N(CH_3)_2$, NC_4H_8O, NC_5H_{10}.

The yields for all R^1, except t-C_4H_9, amount to 81%. The steric hindrance in the case of the t-butyl derivative results in a considerable decrease of the yield (not above 10%).

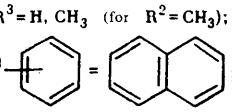
A stereochemical study of the course of the reaction[136-138] showed that compound (CXXXIV) is a mixture of the *erythro*- and *threo*-forms.[133-135] The relative configurations of the diastereoisomers have been established.[137] The authors suggest that the reaction proceeds via a bicyclic transition state in which the nitrogen atom participates and that this is the reason for the observed asymmetric induction.[138] The question of the stability of the transition state is discussed.

VIII. PHOTOCHEMICAL REACTIONS

The authors of a large number of communications[139-153] investigated the photochemistry of β-aminoketones (Mannich bases). The reactions undergone by the latter on irradiation can be divided into the following groups: cyclisations (a), dimerisations (b), isomerisations (c), and other reactions (d). The reactions are shown in the scheme below:



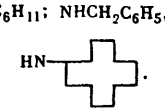
(a) R^1 = H, CH_3, iso-C_3H_7, R^2 = CH_3, C_2H_5, C_6H_5, R^3 = H, CH_3 (for R^2 = CH_3);

(b) R^1 = R^3 = H, R^2 = H, C_6H_5, R^3 = 4-CH_3O, for R^1  ;

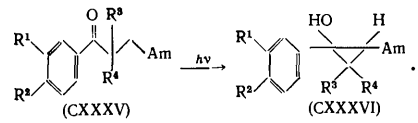
(c) R^1 = R^3 = H, R^2 = H, C_6H_5;

(d) R^1 = H, CH_3, R^2 = R^3 = CH_3;

R^1 = H, R^2 = R^3 = CH_3; $N\begin{smallmatrix}R\\R\end{smallmatrix}$ = $HN(C_3H_7$-iso), $HN(C_4H_9$-t), HNC_6H_{11}; $NHCH_2C_6H_5$,

$NHCH_2CH_2C_6H_5$, NC_4H_8O, NC_5H_{10}, HN—Ad (Ad = adamantyl),  .

The photochemical cyclisation of β-aminopropiophenones (CXXXV) has been reported;[140,142] cyclopropanols were obtained for the first time by this procedure. The cyclisation products (CXXXVI) are indicated in Table 5.

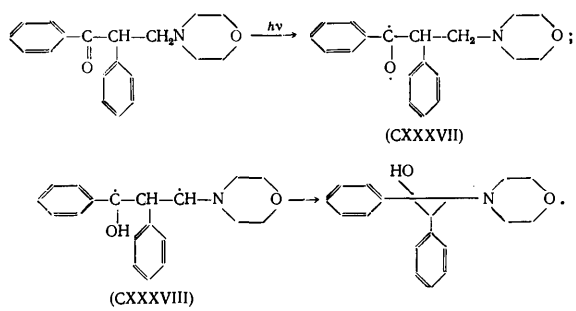


(CXXXV) (CXXXVI)

Table 5. Products of the cyclisation of β-aminopropiophenones (CXXXVI).

R^1	R^2	R^3	R^4	Am	Yield, %	Refs.
H H, CH_3	H H, CH_3, $CH(CH_3)_2$	H CH_3	CH_3, C_6H_5 CH_3	NC_4H_9O $NHCH_3$, NHC_6H_5, $NHCH_2C_6H_5$ $NHCH_2CH_2C_6H_5$	85—98 25—72	[115] [117]

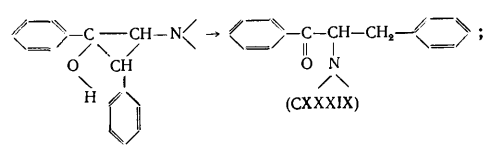
It has been suggested that the excitation of the C = O group results in the initial formation of the C—O biradicals (CXXXVII) which abstract a hydrogen atom from the β-position with the simultaneous formation of the OH group and the C—C biradical (CXXXVIII), which is converted, by intermolecular recombination, into the cyclopropane ring in accordance with the scheme[140]



(CXXXVII)

(CXXXVIII)

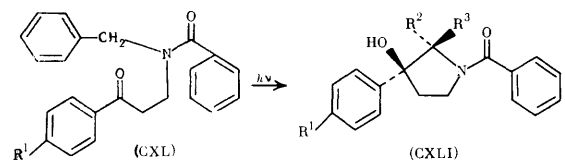
It is of interest that the cyclopropanols (CXXXVI) isomerise to 2-amino-1,3-diphenylpropanones on treatment with alkali or pyridine (CXXXIX):[140,142,143]



(CXXXVI) (CXXXIX)

$N\langle = NC_5H_{10}$, NC_4H_9O.

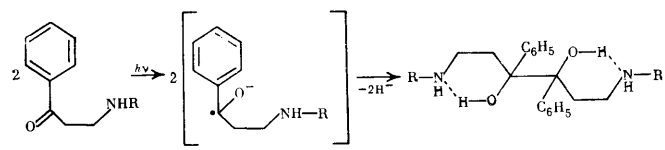
Irradiation of the aminoketones (CXL) in ether gives rise to 1-benzoyl-2-phenyl-3-(4-R-phenyl)pyrrolidin-3-ols (CXLI), which have been resolved into the stereoisomers (2*R*, 3*S*) and (2*S*, 3*R*) by preparative thin-layer chromatography:[144]



(CXL) (CXLI)

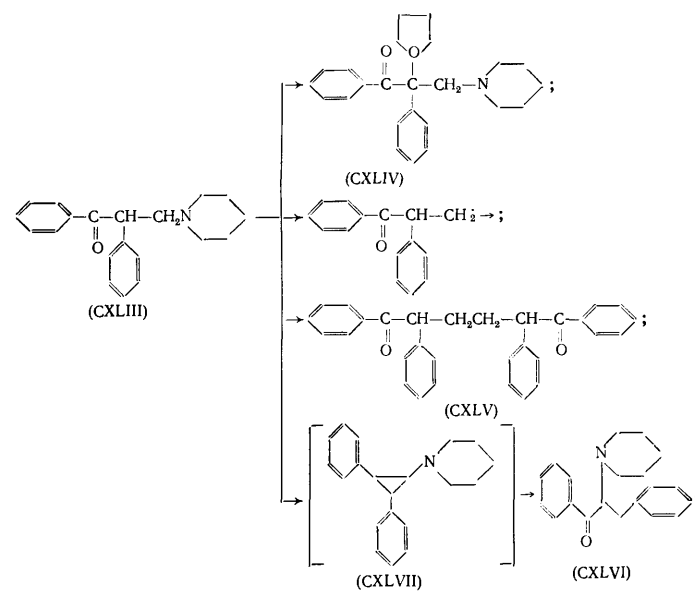
$R^1 = H$, $R^2 = H$, $R^3 = C_6H_5$; $R^1 = Cl$, $R^2 = H$, $R^3 = C_6H_5$;
$R^1 = Cl$, $R^2 = C_6H_5$, $R^3 = H$; $R^1 = Br$, $R^2 = H$, $R^3 = C_6H_5$;
$R^1 = Br$, $R^2 = C_6H_5$, $R^3 = H$ $R^1 = CH_3O$, $R^2 = H$, $R^3 = C_6H_5$.

It is believed[146,147] that photodimerisation with formation of pinacols (the so-called "pinacolisation" reaction) proceeds via the radical-anion(CXLII):



(CXLII)

On irradiation, 2-phenyl-3-piperidinopropiophenone (CXLIII) undergoes different photochemical reactions depending on the solvent:[149]

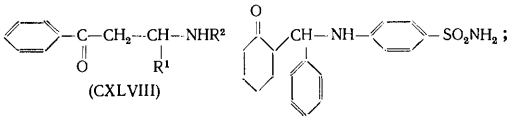


(CXLIII) (CXLIV) (CXLV) (CXLVII) (CXLVI)

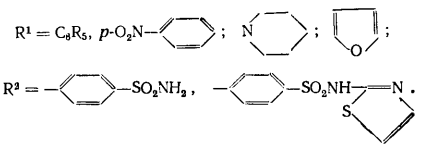
Thus 1,2-diphenyl-3-piperidino-2-(2-tetrahydrofuryl)1-propanone (CXLIV) is formed in tetrahydrofuran (THF). In dioxan, tetrahydropyran, and their mixtures with benzene or in a THF—benzene mixture, compound (CXLIII) gives rise to 1,2,5,6-tetraphenyl-1,6-hexanedione (CXLV) and 1,3-diphenyl-2-piperidino-1-propanone (CXLVI).

The symmetrical diketone (CXLV) is the product of the dimerisation of the radical formed on protolytic elimination of the amine from the initial compound. It is believed[149] that the isomerisation with formation of the α-aminoketone (CXLVI) proceeds via the intermediate cyclopropanol (CXLVII).

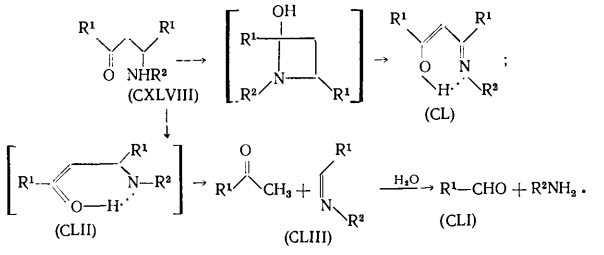
The photochemistry of the sulphamide Mannich bases of the type of compounds (CXLVIII) and (CXLIX) has been investigated:[150]



(CXLVIII) (CXLIX)



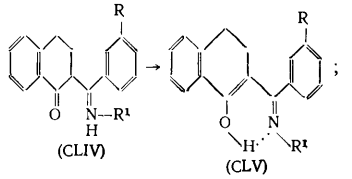
Ultraviolet irradiation of compounds (CXLVIII) in methanol results in the occurrence of two reactions: dehydrogenation to the corresponding β-iminoketones (CL), which exist in the enolic form, and cleavage to the amine, acetophenone, and the aldehyde (CLI):



(CLII) (CLIII) (CLI)

The cyclic intermediate state (CLII), from which acetophenone and the corresponding azomethines (CLIII) are formed, has been proposed for the photolytic cleavage of the aminoketone (CXLVIII).

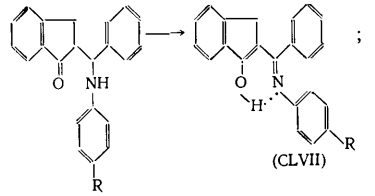
Irradiation of the Mannich bases (CLIV) with ultraviolet light leads to 2-[(*N*-R^1-imino)(4′-R-phenyl)]methyl-3,4-dihydro-1-naphthols (CLV):[152]



(CLIV) (CLV)

R=H, NO_2, R^1=C_6H_5, *p*-$CH_3OC_6H_4$, α-naphthyl.

2-[(4′-R-Phenylimino)phenyl]methyl-1-indenols have been obtained from compounds (CLVI) under analogous conditions:



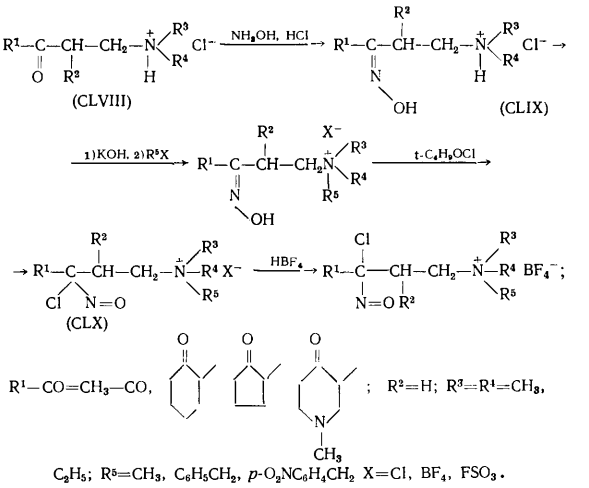
(CLVI) (CLVII)

R=H, CH_3O.

IX. OTHER REACTIONS

It has been shown[154] that the β-aminoketones obtained by the aminomethylation of 1-tetralone, 3,3,6,7-tetramethyl-1-tetralone, acetophenone, 1-chromanone, and *N*-methyl-4-piperidinone with piperidine are capable of producing on acetolysis unsaturated ketones, which are slowly converted into dimers.

The Mannich bases (CLVIII) have been converted into the oximes (CLIX), which were then oxidised to the *gem*-chloro-nitroso-derivatives (CLX) by the chloronium ion:[155]



(CLVIII) (CLIX) (CLX)

C_2H_5; R^5=CH_3, $C_6H_5CH_2$, *p*-$O_2NC_6H_4CH_2$ X=Cl, BF_4, FSO_3.

Complexes with lanthanide metal ions have been obtained from β(α)-naphthylamino-2,4,6-dihydroxypropiophenones;[156] a "metal–metal" bond has not been observed in these complexes, which indicates their monomeric nature.

The influence of 5-substituted 2-hydroxy-β-morpholinopropiophenones and *NN*-bis[β-(2-hydroxy-5R-benzoyl)ethyl]-piperazines on the resistance of polyethylene to the action of the atmosphere under the conditions of accelerated ageing has been investigated.[157] Despite their low effectiveness as thermal stabilisers, they are good light stabilisers of polyethylene.

Aminoketones have been finding applications also in the preparation of various polymers.[3c,55,56,75,76,127,158]

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Metallocarbaboranes. Structural Studies in Recent Years

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Structural studies on metallocarbaboranes (MCB) are surveyed and modern theoretical ideas about the electronic structure of cluster and particularly polyhedral MCB systems are discussed. The characteristic features of the geometry of the polyhedra in specific MCB are examined in connection with the specific features of their electronic structure.
The bibliography includes 78 references.

CONTENTS

I. Introduction 515
II. Modern ideas about the electronic structure of metallocarbaboranes 516
III. The structures of metallocarbaboranes 517

I. INTRODUCTION

Metallocarbaboranes (MCB) constitute a large class of polyhedral compounds which contain, together with boron and carbon atoms, also several metal atoms in the polyhedron. These compounds, which occupy an intermediate position at the junction between organoelemental and organometallic chemistry, have become in recent years the objects of vigorous research. As frequently happens, the results obtained in this boundary field of science are not only of independent importance but to a large extent they have enriched the ideas which have arisen in adjacent disciplines and have frequently stimulated their development. Such a stimulating role in relation to the chemistry of cluster compounds was played at one time by MCB, which became, as early as the middle of the 1960's, one of the first examples of metal-containing polyhedral systems. The studies in this field have made it possible to combine successfully the researches into the complex and unexpected reactions and far-reaching thermal rearrangements with the synthesis of a large number of extremely stable compounds which are promising from the practical standpoint.

The specific features of MCB are determined in the first place by their unusual polyhedral structures, which are distinguished by an usually wide variety and frequently by their aesthetic perfection. It is therefore natural that in the investigation of these compounds structural studies (these are carried out almost exclusively by X-ray diffraction) occupy in a certain sense a central position, because, on the one hand, they provide the necessary information without which it would be impossible to plan and achieve the synthesis of MCB and, on the other hand, they serve as a basis for the development and improvement of theoretical ideas about their structure.

The following figures reveal the rate of growth of the number of structural studies on MCB in recent years. Thus the exhaustive review by Grimes,[1] which covers the literature up to 1975, quotes a list of more than 400 compounds synthesised by that time, of which only 46 have been subjected to structural studies; at the beginning of 1981, 95 X-ray

diffraction studies on MCB had been performed and during the last 1.5–2 years a further 25 studies concerned with this field have been published.

As a result of the wide variety of the structures of MCB, in many of these studies not only was the structure of the newly synthesised compound established but also new types of polyhedra, unusual modes of coordination of the metal atoms, or hitherto unknown motifs in the disposition of the atoms in the polyhedron were discovered. Although less than 20 years have elapsed since the synthesis of the first MCB by Hawthorne and co-workers[2] in 1965, definite theoretical ideas have already been formulated, which, while they do not always possess an adequate predictive power, at any rate make it possible to generalise and arrange systematically the experimental data accumulated at the present time. Here we have in view the rules for the evaluation of the numbers of skeletal electrons (i.e. the electrons responsible for the bonding in the polyhedron), sometimes referred to as Wade's rules, or the "$2n + 2$" rules.[3] The important role of these rules for the elucidation of the structures of cluster compounds in general and the wide variety of polyhedral boron derivatives in particular has been examined in a number of studies (see, for example, Refs. 3–7). The essential features of Wade's ideas are briefly described in this review in order to employ them subsequently in considering the MCB structures.

II. MODERN IDEAS ABOUT THE ELECTRONIC STRUCTURE OF METALLOCARBABORANES

The ideas underlying the "$2n + 2$" rule have been described in a most logical and readily understood form in the book of King and Rouvray,[5] who consider the structure of cluster systems from the standpoint of the topology of the polyhedron. According to their description, each boron or carbon atom (for simplicity, we shall consider initially a purely carbaborane polyhedron) in an n-vertex polyhedron have an outer atomic orbital (AO), which is used to form the exopolyhedral bond, two tangential orbitals directed along the tangent to the envelope of the polyhedron, and one internal orbital directed towards the centre of the polyhedron (the inner and outer orbitals can be regarded, for example, as two sp-hybrid orbitals). When a cluster is formed, the exopolyhedral orbitals (n orbitals) are not involved and the interaction of $2n$ tangential AO leads to n bonding and n antibonding cluster orbitals.[5] It remains to explain what happens to the n inner orbitals.

In comparing "superaromatic" three-dimensional clusters with planar aromatic systems (here a comparison is made of the sp^2-hybrid orbitals involved in the formation of the σ-bonds of the aromatic ring with the tangential orbitals and of the unhybridised p orbitals with the inner orbitals of the cluster atoms), King and Rouvray[5] emphasise the important topological difference between these two types of aromatic systems. The planar systems are characterised by cyclic graphs C in which each atom is linked to only two neighbours, while the so-called complete graphs K_n, in which each atom is assumed to be bound to all the remaining atoms, are characteristic of the cluster polyhedra. This topological difference is responsible for the different forms of the quantum-chemical equations—for example, the different matrices of the linear equations in the simple Hückel method (only the non-diagonal elements in these matrices, which correspond to pairs of atoms between which there is a chemical bond, are known to be non-zero). The solution of these equations shows that, in contrast to planar molecules, for example, those of benzene (where the interaction of six "inner" p orbitals gives rise to three bonding and three antibonding π orbitals), in the three-dimensional systems the interaction of the n inner orbitals leads to only one non-bonding cluster orbital and $n - 1$ antibonding orbitals.

Thus the total number of the bonding MO in an n-vertex cluster is $n + 1$ (n orbitals formed by the tengential AO and one formed by the inner AO). This approach provides a clear explanation of the experimental rule[3] according to which the most stable carbaboranes, with the maximum delocalisation of electron density, have $2n + 2$ skeletal electrons, which are responsible for the bonding in the polyhedron. Such polyhedra have only triangular faces; they are referred to as *closo*(closed)-polyhedra or deltahedra.

When one of the vertices of the *closo*-polyhedron is removed, one (open) (non-triangular) face arises in the latter. The resulting polyhedron can be regarded as a combination of two complete graphs, one of which includes only inner vertices i.e. those not located on the "open" face, and the other only the boundary vertices (belonging to the "open" face). The interaction of the inner orbitals of the atoms belonging to each graph results in the formation of one additional bonding orbital in each instance. Thus the total number of binding orbitals formed by the interaction of both tangential and inner orbitals in such instances is $n + 2$, where n is the number of vertices of the polyhedron. Such polyhedra with one "open" face are referred to as *nido*-polyhedra (from the Greek "nido"—nest). The so-called *arachno*-structures (from the Greek "arachne"—cobweb) with $2n + 6$ skeletal electrons can be obtained by the removal of two vertices from *closo*-systems.

Thus the opening of the polyhedron, namely the formation of *nido*- and *arachno*-systems, corresponds to an excess of skeletal electrons (relative to $2n + 2$). A deficiency of skeletal electrons can also affect the character of the cluster polyhedron, leading to the formation of extremely unusual structures in which one or several triangular faces have over their centres additional vertices (caps). These polyhedra can also be formally classified as *closo*-systems, because they contain only triangular faces. However, in contrast to the polyhedra representing "normal" $2n + 2$ electron clusters, polyhedra with additional vertices can be subdivided into two smaller *closo*-polyhedra (for example, along the planes of the faces over which the caps are centred). Certain "super-electron-deficient" systems of this kind will be discussed below.

Table 1. The numbers of electrons supplied to the MCB polyhedron by various groups.

Group	No. of electrons	Group	No. of electrons
BH	3—1=2	$Fe(CO)_3$	8+6—12=2
CH	4—1=3	CoCp	9+5—12=2
PMe	5—1=4	$RhH(PPh_3)_2$	9+1+4—12=2
$Re(CO)_3$	7+6—12=1	$NiC_2B_9H_{11}$	10+4—12=2
FeCp *	8+5—12=1	$Pt(PPh_3)_2$	10+4—12=2
$CoC_2B_9H_{11}$	9+4—12=1	NiCp	10+5—12=3
$Rh(PPh_3)_2$	9+4—12=1	$AuC_2B_9H_{11}$	11+4—12=3

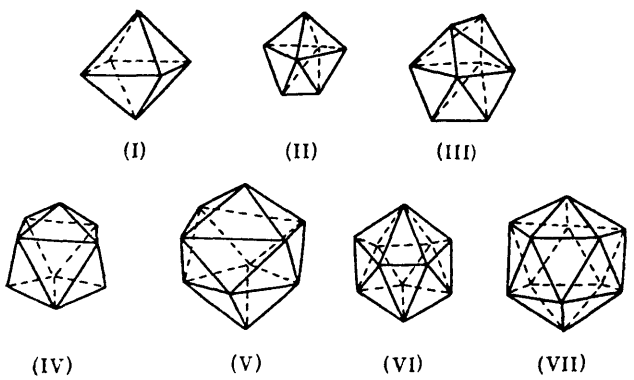
*Here and henceforth Cp = cyclopentadienyl.

In conclusion of this Section, one may indicate how the numbers of skeletal electrons in specific, particularly polyhedral, MCB systems should be evaluated (Table 1). It is

evident from the foregoing that the BH and CH groups each supply three orbitals and correspondingly two and three electrons to the polyhedron. When a transition metal atom is incorporated in the polyhedron, it is assumed that, of the nine of its orbitals, it employs three for bonding in the polyhedron, while the remaining six are used to form bonds with external ligands. It is assumed that the electrons of the metal and the ligands fill in the first place the orbital not involved in the bonding within the polyhedron, i.e. the six outer orbitals. The ML_n group therefore supplies to the polyhedron x electrons of the metal and k electrons of the n ligands, while 12 electrons are distributed among the exopolyhedral orbitals. Thus, overall, the group ML_n supplies $x + k - 12$ skeletal electrons to the polyhedron. For example the $Fe(CO)_3$, CoCp, $Pt(PR_3)_2$, etc. groups function, like the BH group, as donors of two electrons, while the NiCp group, like the CH group, supplies three electrons to the polyhedron.

III. THE STRUCTURES OF METALLOCARBABORANES

We shall now proceed directly to the discussion of the structures of the MCB. The ideal *closo*-polyhedra characteristic of the $B_nH_n^{2-}$ ions and carbaboranes with $n = 6 - 12$ are presented below (Table 2).



The polyhedra of the MCB and carbaboranes having the same number of vertices are usually analogous, although the introduction of a metal atom normally reduces the symmetry of the polyhedron relative to the corresponding carbaboranes. In a number of instances new skeletons, without analogues in the structural chemistry of boranes and carbaboranes, have been discovered in MCB: however, for their description it is frequently also convenient to begin with the *closo*-systems listed in Table 2.

Table 2. *closo*-Polyhedra characteristic of the $B_nH_n^{2-}$ ions and the carbaboranes $C_2B_{n-2}H_n$.

No.	Ion	Polyhedron	Symmetry group	No. of vertices	No. of edges	No. of faces
(I)	$B_6H_6^{2-}$	Octahedron	O_h	6	12	8
(II)	$B_7H_7^{2-}$	Pentagonal bipyramid	D_{5h}	7	15	10
(III)	$B_8H_8^{2-}$	Dodecahedron	D_{2d}	8	18	12
(IV)	$B_9H_9^{2-}$	Three-cap trigonal prism	D_{3h}	9	21	14
(V)	$B_{10}H_{10}^{2-}$	Two-cap square antiprism	D_{4d}	10	24	16
(VI)	$B_{11}H_{11}^{2-}$	Octadecahedron	C_{2v}	11	27	18
(VII)	$B_{12}H_{12}^{2-}$	Eicosahedron	I_h	12	30	20

We shall next consider MCB structures with different numbers n of vertices in the polyhedron; only the most characteristic and typical examples, and not all the structures investigated, are quoted for each value of n. A more complete idea about the MCB structures can be obtained from a number of previous reviews.[1,8-15]

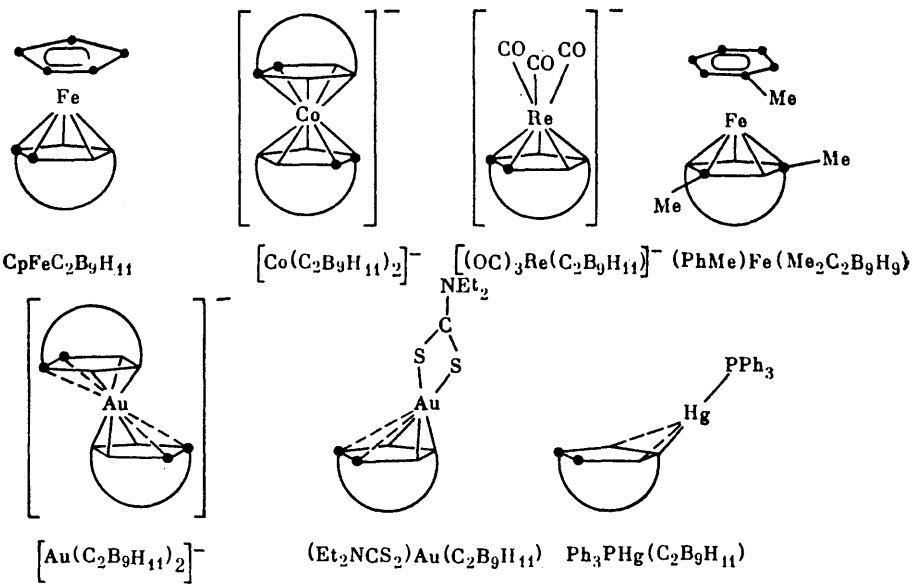


Figure 1. 12-Vertex MCB;[16-23] for simplicity, the *nido*-eicosahedral fragments are represented by half-circles.

1. The Highest (12- and 13-Vertex) Metallocarbaboranes

The most extensive and most widely investigated class of MCB comprises the eicosahedral 12-vertex MCB (Fig.1)†. The first MCB whose structure has been investigated, namely $CpFeC_2B_9H_{11}$, which has a sandwich structure, belongs to this class.[16] Its iron atom is symetrically coordinated to the cyclopentadienyl ligand and to the "open" pentagonal C_2B_3 face of the dicarbollide $(C_2B_9H_{11})^{2-}$ ligand; the Fe–C and Fe–B distances are identical within the limits of the accuracy of the measurement and amount to 2.04 Å.

Subsequently a large number of 12-vertex MCB, incorporating the metals of almost all the Groups in the Periodic System, were synthesised; more than 40 of these have been studied by X-ray diffraction. Almost all the 12-vertex metallocarbaboranes have a more or less strongly distorted eicosahedral structure and, in contrast to the iron derivatives menticned above, in most cases are diamagnetic complexes satisfying Wade's rule. As an example, one may quote two MCB investigated in the form of caesium salts—the anions $[Co(C_2B_9H_{11})_2]^-$ [17] and $[(OC)_3Re(C_2B_9H_{11})]^-$,[18] which belong to the class of MCB known for the longest time, and also the π-arene complex of bivalent iron $(MePh)Fe(Me_2C_2B_9H_9)$ synthesised several years ago.[19] A fully symmetrical coordination of the metal atom to the π-dicarbollide ligand was observed in these compounds. However, such symmetrical coordination is by no means always observed in the 12-vertex MCB. Thus, on passing from the d^6 and d^7 complexes of iron(II), cobalt(III), and rhenium(I), etc. to the d^8 complexes of palladium(II), platinum(II), and gold(III) and further to the d^{10} derivatives of mercury(II), considerable distortion of the symmetrical coordination is observed, being reflected in a shift of the metal atom towards the B atoms of the "open" face and in the breakdown of its planarity, which promotes a shift of carbon atoms away from the metal atom and a shortening of the C–C bond in the *ortho*-dicarbollide ligand. Such distortion of the coordination of the carbaborane ligand can be called the "shift" distortion and in the case of the *ortho*-dicarbollide ligand the "pseudo-π-allyl" distortion.

For example, the difference between the Au–B and Au–C distances in the anion $[Au(C_2B_9H_{11})_2]^-$ [20] reaches approximately 0.5 Å, the angle of inflection in the "open" face along the B...B line is 13.6°, and the C–C bond is shortened to 1.46 Å. As a result of the further "opening" of the MCB polyhedron on passing to the mercury derivative $Ph_3PHg(C_2B_9H_{11})$,[21] the metal atom is bound to only one B atom in the "open" face (the Hg–B distance is 2.20 Å), while the binding to its neighbours in the face assumes the character of weak interaction (with Hg...B distances of 2.50 and 2.53 Å). Finally, the thallium complex can be regarded as the double salt $[R_4P]^+Tl^+[C_2B_9H_{11}]^{2-}$ rather than the phosphonium slat of the thallium-carbaborane anion (Tl...B = 2.664–2.744 Å and Tl...C = 2.915 Å[22]).

It must be emphasised that the above distortions of the *closo*-structure are observed under conditions where the "$2n + 2$" rule formally holds and are independent of whether or not the 18-electron rule holds for the coordination of the metal atom. This is indicated by the structural data for the two gold complexes presented in Fig.1, namely $[(Et_2NCS_2)_2Au]^+[(Au(C_2B_9H_{11})_2]^-$ [20] and $(Et_2NCS_2).Au(C_2B_9H_{11})$,[23] in which identical pseudo-π-allyl distortions are observed, although in the former the Au atom has a 20-electron shell whereas in the latter it has an 18-electron shell. The only structural investigation of the platinacarbaborane $Pt(C_2B_9H_{11})_2$, incorporating the Pt atom in the +4 oxidation state, carried out hitherto[24] has shown that the distortions in the polyhedron are determined evidently solely by its electronic configuration and not by the presence in it of a specific metal atom. Indeed, in the d^6 complex indicated the platinum atom is included in two eicosahedra which are actually symmetrical: the average Pt–C and Pt–B distances are 2.24 and 2.20 Å respectively.

The nature of the "shift" distortions in the symmetrical coordination of the metal in the 12-vertex MCB has been studied in two investigations,[25,26] in which calculations were carried out for the interaction of the $Pt(PH_3)_2$ fragment with the borate anion $B_{11}H_{11}^{2-}$ and its carbaborane analogues by the extended Hückel method (Fig.2). The calculation showed that the character of the coordination of the metal atom as well as the orientation of the PtP_2 group relative to the ligand are determined by the interaction between the highest occupied molecular orbital (HOMO) in this group (i.e. the hybridised d_{xz}-p_x orbital localised in the plane of the Pt–P bonds) and the lowest unoccupied MO (LUMO) of the ligand. In the borate anion $B_{11}H_{11}^{2-}$ two electrons are located at the doubly degenerate $5e_1$ level. As a result of the replacement of one or two B atoms in the "open" face by C atoms, the degeneracy is removed and the location of the nodal plane of the LUMO depends on the positions of the carbon atoms in the carbaborane ligand. The optimum overlap of the HOMO of the metal and the LUMO of the ligand occurs for the orientation in which their nodal planes coincide.

The HOMO nodal plane of the $Pt(PH_3)_2$ fragment is perpendicular to the PtP_2 plane and the ML_2 fragment should therefore be at right angles to the symmetry plane of the $CB_{10}H_{11}$ (I) and *ortho*-$C_2B_9H_{11}$ (III) ligands (Fig.2) and parallel to this plane in the case of the *meta*-$C_2B_9H_{11}$ (II) ligand. Such orientation does actually obtain in the three palladium and platinum complexes whose structures have been investigated: $(Me_3CNC)_2Pd(1\text{-}Me_3NCB_{10}H_{10})$,[27] $(PhMe_2P)_2Pt(2,5\text{-}Me_2C_2B_9H_9)$,[28] and $(Et_3P)_2Pt(3,4\text{-}C_2B_9H_{11})$.[25]

Fig.2 illustrates yet another, perhaps even more important conclusion reached in the above studies.[25,26] Calculation has shown that the LUMO of the carbaborane ligand is localised at the B atoms to a much greater extent than at the C atoms. This factor explains qualitatively the "shift" distortions of the MCB eicosahedra observed for the 12-vertex complexes of metals with the d^8–d^{10} electron configuration.

The most realistic prospects, at the present time, for the practical application of the MCB are also associated with the largest and most thoroughly investigated class of MCB, namely the 12-vertex complexes. Several years ago a structural study was made[29] on the rhodium hydride complex $(Ph_3P)_2PhH(C_2B_9H_{11})$—an effective homogeneous catalyst for the hydrogenation of olefins. A study of the catalytic properties of this complex established that the rate of the hydrogenation reaction diminishes after the addition of free triphenylphosphine to the reaction mixture. The authors[29] suggested that the catalytic hydrogenation reaction takes place with participation of a coordination-unsaturated metal atom and that the first, rate-limiting stage of the catalytic process involves the elimination of the Ph_3P ligand.

These ideas were used for the specific synthesis of a new rhodiacarbaborane complex with a still higher catalytic activity. In the new compound $(Ph_3P)HRhC_2B_9H_{10}C_4H_7)$, whose structure has also been studied,[30] the rhodium atom is involved in η^2-type coordination to the double bond of the butenyl substituent of the dicarbollide ligand (Fig.3). The η^2-coordinated double bond, activated by the interaction with the rhodium atom, is hydrogenated in the first place

†The carbon atoms in Fig.1 and also in some of the subsequent figures are designated by filled circles.

under the conditions of the hydrogenation reaction. Subsequently the metal atom becomes coordination-unsaturated, which in fact determines the catalytic properties of the complex. Indeed the complex described proved to be one of the most effective catalysts for the homogeneous hydrogenation of olefins known at the present time. The related alkene-substituted carbaborane rhodium hydride complex $(PH_3P)_2HRhC_2B_9H_9C_8H_{14}$), with an unsaturated exopolyhedral nine-membered ring, whose double bond is coordinated to the metal atom (Fig. 3), exhibits a somewhat smaller catalytic activity.[31]

Yet another rhodium complex showing a catalytic activity, namely $(Ph_3P)_2HRhC_2B_{10}H_{12}$ (Fig. 4),[32] belongs to the group of the very few structurally characterised 13-vertex MCB.

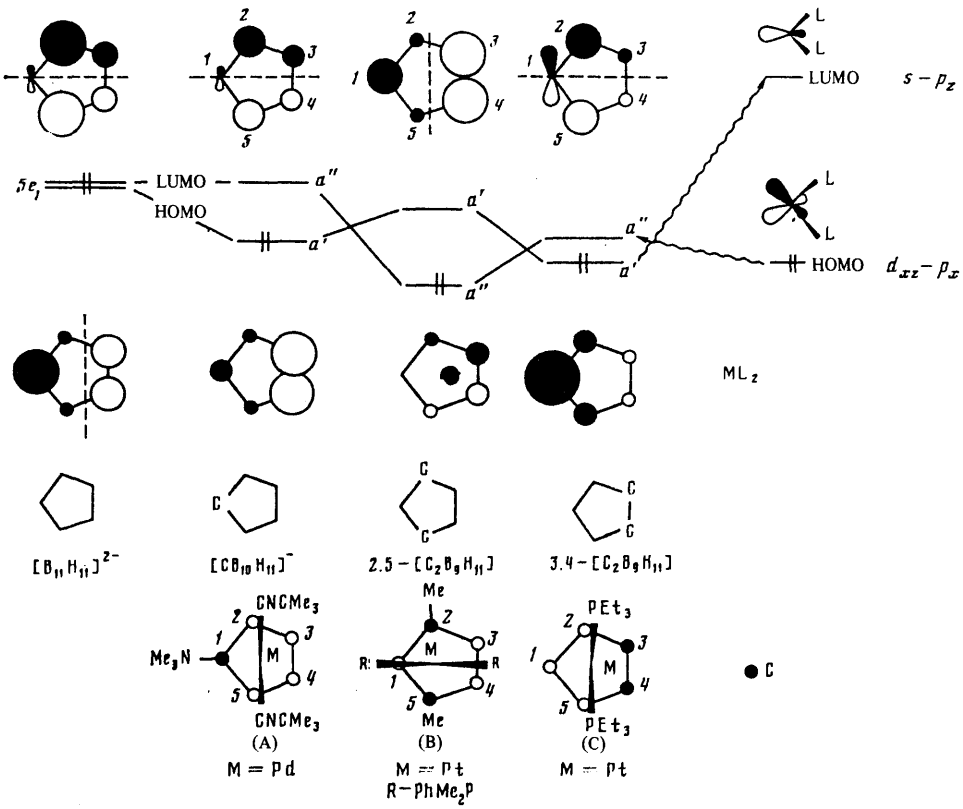
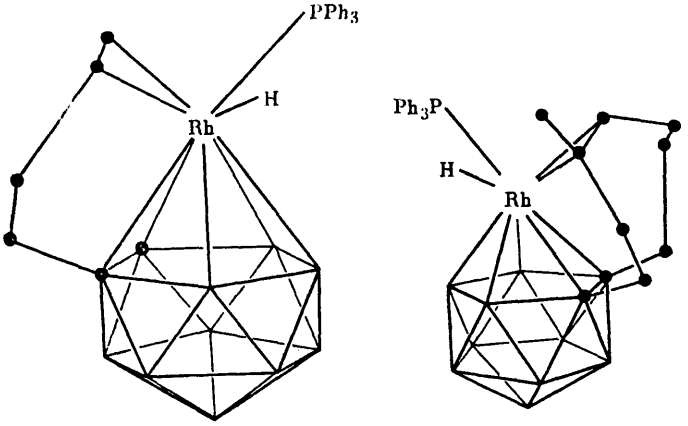


Figure 2. Comparison of the results of theoretical[25,26] and experimental[25,27,28] studies of the geometrical features of the molecules of 12-vertex MCB.

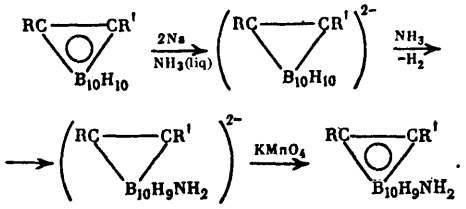
These complexes contain the so-called docosahedral polyhedron in which, in contrast to the eicosahedron, the "open" pentagonal face coordinating the metal atom has been replaced by a hexagonal face. Structural studies on the 13-vertex complexes of cobalt, i.e. $CpCoC_2B_{10}H_{12}$,[33] and titanium, i.e. $[Me_4N]_2[Ti(Me_2C_2B_{10}H_{10})_2]$,[34] with a docosahedral structure are important for the understanding of the mechanisms of certain reactions of the series of *o*- and *m*-carbaborane derivatives.



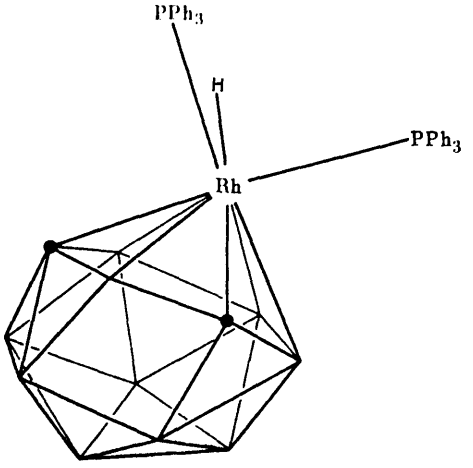
$(Ph_3P)HRhC_2B_9H_{10}C_4H_7$ $(Ph_3P)HRhC_2B_9H_9C_8H_{14}$

Figure 3. The structures of 12-vertex alkenerhodium hydride complexes—catalysts of the homogeneous hydrogenation of olefins.[30,31]

In 1967 Soviet workers proposed an effective method of synthesis of B-substituted derivatives of *o*-carbaborane by treating with nucleophiles the products of the reduction of *o*- and *m*-carbaborane derivatives with a solution of sodium in liquid ammonia (see Kalinin's review[35]). It is suggested that this process proceeds via the intermediate stage of dicarbadodecaborate(14) dianions:



The dicarbadodecaborate anion is also formed on reduction of *o*-carbaborane by metallic sodium in THF in the presence of catalytic amounts of naphthalene. The introduction of transition metal salts ($CoCl_2$ and $TiCl_4$) into the reaction mixture made it possible to isolate the derivatives of the dicarbadodecaborate anion in a pure form and to investigate their structure.[33,34] It may be hoped that detailed studies of the 13-vertex MCB will lead in the future to the possibility for a more detailed investigation of the mechanism of this reaction, which is exceptionally important for the chemistry of *o*- and *m*-carbaboranes and also will make it possible to explain the preferential formation of only some of the isomers of its final complex which are possible in principle.



$(Ph_3P)_2HRhC_2B_{10}H_{12}$

Figure 4. The structure of $(Ph_3P)_2RhH(C_2B_{10}H_{12})$.[32]

2. 11-Vertex MCB

The geometry of the octahedron is characteristic of 11-vertex *closo*-MCB (Fig.5). Many 11-vertex MCB, whose structures have been investigated, for example, the cobaltacarbaborane $CpCoC_2B_8H_9Br$ which we have studied,[36] can be regarded as resulting from the coordination of the metal atom to the non-planar hexagonal "open" face of the boron–carbon skeleton, which resembles a basket and is well-known in the chemistry of boron as the decaborane-14 ($B_{10}H_{14}$) skeleton. In contrast to the eicosahedron, in which each vertex has five nearest neighbours in the polyhedron, in the octadecahedron with pentacoordination (here and henceforth the coordination number C.N. is understood as the number of nearest neighbours in the polyhedron) there are two tetracoordinate and one hexacoordinate vertices. Numerous studies of the structures of MCB with polyhedra having non-isotypical vertices and also investigation of the thermal rearrangements in these systems[9] have shown that the isomers in which the carbon atoms occupy the vertices with the lowest C.N. and the metal atoms occupy those with the highest C.N. are as a rule thermodynamically most stable. A good illustration of this finding is provided by the structure of the bimetallic 11-vertex MCB $Cp_2FeCoC_2B_7H_9$ in the octadecahedral polyhedron of which two carbon atoms occupy tetracoordinate vertices and the iron and cobalt atoms occupy respectively hexacoordinate and pentacoordinate vertices. In this molecule there are 23 skeletal electrons instead of the 24 expected for *closo*-MCB, which causes, according to the authors of the structural study,[37] certain geometrical distortions (differences between the lengths of chemically equivalent B–B bonds amounting to approximately 0.10 Å have been observed), which leads to the loss of a plane of

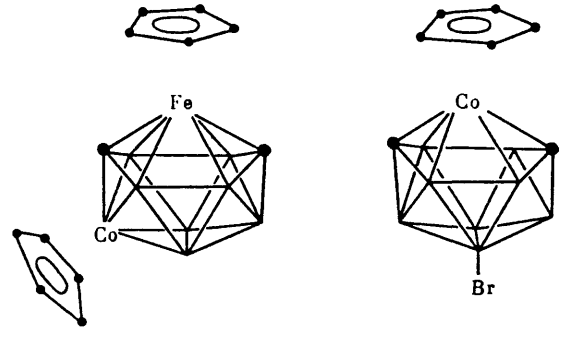
symmetry by the $FeCoC_2B_7$ polyhedron. However, it is noteworthy that the lack of one electron does not affect the geometry of the iron cyclopentadienyldicarbollyl complex $CpFeC_2B_9H_{11}$.[16]

The difference between the C.N. of the atoms in the polyhedron influences the lengths of the bonds in which they are involved. This difference makes it possible, for example, to account for the significant (up to approximately 0.3 Å) difference between the Co–C and Co–B distances in $CpCoC_2B_8H_9Br$. On the other hand, the increase of the Pt–B distance to 2.60–2.66 Å compared with the Pt–C bond, which is 2.17 Å long in the complex $(Ph_3P)_2PtC_2B_8H_{10}$,[38] can be hardly accounted for solely by the influence of the difference between the C.N. of the B and C atoms. This becomes even more evident in relation to another 11-vertex platinacarbaborane, namely $(Me_3P)_2PtC_2B_8H_{10}$.[39] Although this complex contains 24 skeletal electrons, it has in fact a *nido*-eicosahedral structure and not an octadecahedral structure, but its polyhedron can in fact be regarded as a highly distorted octadecahedron in which the metal atom is very markedly displaced relative to the symmetry plane of the polyhedron. As a result, the distances from the platinum atom to the most remote boron and carbon atoms in the "formally open face" of the octadecahedron (3.10 and 2.82 Å) altogether do not correspond to a valence interaction.

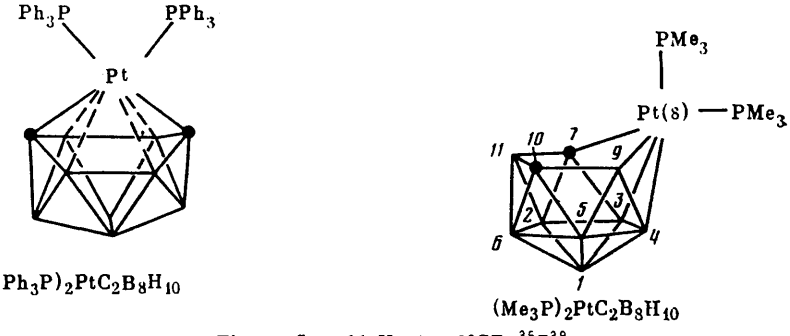
Although the 11-vertex MCB have been investigated in much less detail than the 12-vertex compounds, the few examples examined have already shown that here too the same rule apparently holds as for the eicosahedral MCB: the incorporation of a metal atom with a d^8 configuration leads to the "loosening" of the polyhedron and sometimes, as, for example, in the last platinacarbaborane considered above,[39] also to a decrease of its symmetry. It will be shown below that this rule holds likewise for the lowest MCB.

3. 10-Vertex MCB

The 10-vertex *nido*-carbaboranes, having the decaborane-14 skeleton, which have been investigated in fair detail, are structurally very close to the 11-vertex MCB with an octadecahedral polyhedron. Like each of the BH groups, the



$Cp_2FeCoC_2B_7H_9$ $CpCoC_2B_8H_9Br$



$(Ph_3P)_2PtC_2B_8H_{10}$ $(Me_3P)_2PtC_2B_8H_{10}$

Figure 5. 11-Vertex MCB.[36–39]

CpCo group in the cobaltacarbaborane $CpCo(C_2B_7H_{11})$[40] (Fig.6) behaves, as usual, as the donor of two electrons, while the two CH groups supply three electrons each to the polyhedron; the bridging hydride atoms, whose location has been objectively identified in a structural study,[40] serve as a source of further two electrons. Overall, the complex contains 24 skeletal electrons and has the structure of a 10-vertex *nido*-polyhedron.

Whereas the metal atom in the cobalt complex occupies, as was to be expected, a high-coordination site in the "open" face, in the nickel derivative $(Et_3P)_2Ni(Me_2C_2B_7H_9)$[41] and the platinum derivative $(Ph_3P)_2Pt(CB_8H_{12})$[42] with an analogous skeleton the metal atom occupies a low-coordination site. The coordination of the metal atom in this low-coordination site in the "open" face constitutes a model in a certain sense (assuming that the metal atom is coordinated to the centres of the edges of the polyhedron) of the square-planar environment characteristic of the usual nickel(II) and platinum(II) complexes.

The second low-coordination site in the "open" face of 10-vertex *nido*-complexes of nickel and platinum is occupied by a carbon atom, which, together with the exopolyhedral ligand (the Me group in the nickel complex and the hydrogen atom in the platinum compound), turned "to the outside" of the polyhedron, contains also the so-called "axial" hydrogen atom directed towards the centre of the "open " face. The question arises how one should take into account this carbon atom in calculating the number of skeletal electrons. If both its substituents are regarded as exopolyhedral, then the given carbon atom should serve as a donor of two (4−2 = 2) electrons. In this case the 10-vertex *nido*-polyhedron contains 22 skeletal electrons, i.e. two electrons less than would be necessary to satisfy Wade's "2*n* + 4" rule. This discrepancy is entirely reasonable because, according to Wade's rule, each atom employs three orbitals for the bonding in the polyhedron (see above), while the above discussion assumes that the C(9) and C(6) atoms in the nickel and platinum complexes respectively employ only two orbitals for the bonding in the polyhedron. If, on the other hand, it is assumed that the H_{ax} atom is not an exo-substituent in the full sense of the term and is involved in the bonding within the polyhedron (for example, in the weak interaction with the neighbouring, in relation to the carbon atom, boron atoms in the "open" face), then in this instance both electrons of the $C-H_{ax}$ bond can be classified as the skeletal electrons of the complex. Thus the total number of skeletal electrons

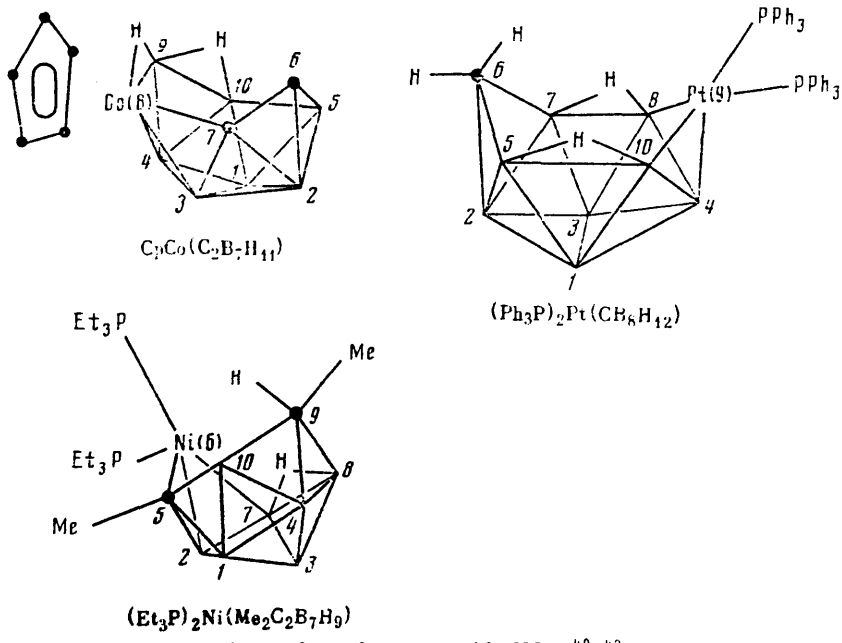


Figure 6. 10-Vertex *nido*-MCB.[40–42]

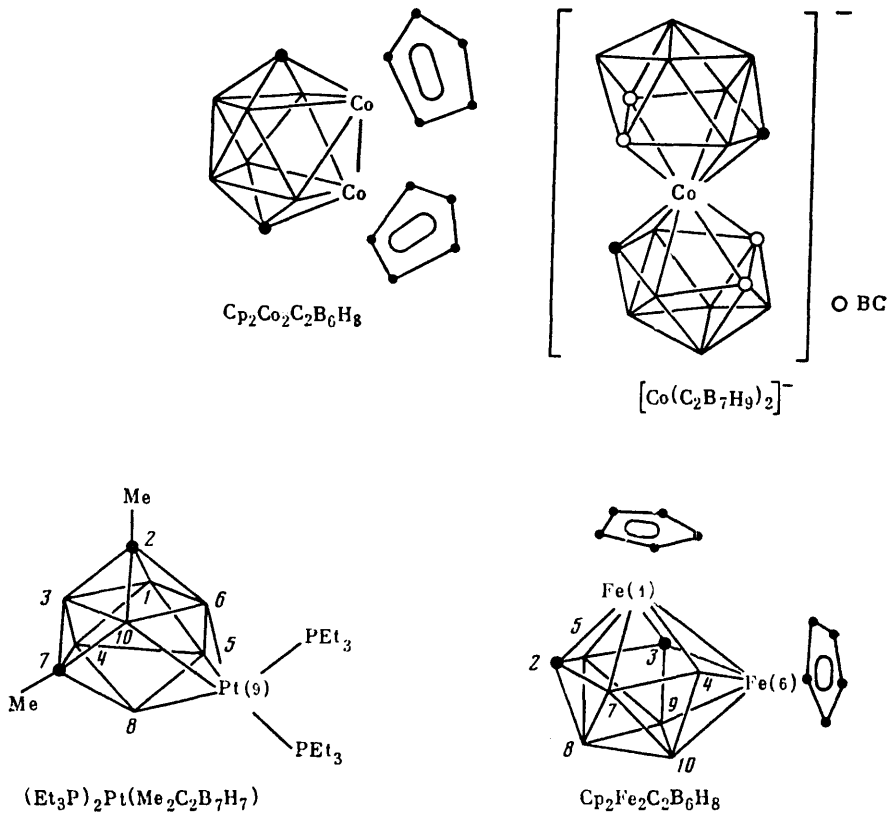


Figure 7. 10-Vertex *closo*-MCB.[43–46]

in the nickel and platinum derivatives under discussion is 24 and is consistent with the *nido*-geometry of the 10-vertex complex.

The "basic" polyhedron in 10-vertex *closo*-MCB is the so-called two-cap square antiprism centred with respect to the faces of both bases (Fig. 7). Polyhedra having this structure have been found in structural studies on cobaltacarbaboranes—the bimetallic complex $Cp_2Co_2C_2B_6H_8$ [43] and a *commo*-MCB—the $[Co(C_2B_7H_9)_2]^-$ anion#.[44] It is striking that the metal atoms in both compounds occupy vertices in the "equatorial" belt of the antiprism, whiole the low-coordination positions in the "caps" are occupied preferentially by carbon atoms.

As in the MCB with a larger number of vertices discussed above, the 10-vertex cobaltacarbaboranes (with a d^6 configuration of the metal atom) have a fairly symmetrical structure. On the other hand, in the platinacarbaborane $(Et_3P)_2Pt(Me_2C_2B_7H_7)$[45] ($d^8$ configuration), which, like its cobalt analogues, satisfies Wade's rule, appreciable distortions of the polyhedron are observed. They are expressed in the formation of a tetragonal open face C(7)B(8)Pt(9)B(10), which arises as a result of the dissociation of one of the "equatorial" bonds [Pt(9)...C(7) bonds 2.83 Å long] in a two-cap square antiprism.

In discussing the structure of 10-vertex MCB, one must not fail to mention the structure of the very interesting bimetallic iron complex $Cp_2Fe_2C_2B_6H_8$.[46] The geometry of the diamagnetic molecule can be described only approximately as one corresponding to a two-cap square antiprism. For the purpose of this description, one must imagine that one "equatorial" bond C(3)–B(4) in the antiprism has been broken and one of the "caps" [Fe(6)] is linked directly to the metal atom in the "equatorial" belt remote from it [the Fe(6)–Fe(1) bond 2.571 Å long].

Such structural anomalies are evidently due to the insufficiency of skeletal electrons for the construction of a 10-vertex *closo*-system. In the given complex there are 20 (instead of 22) electrons, which is the reason for their unusual structure. Although formally this compound belongs to the class of 10-vertex *closo*-MCB (with all the faces triangular), in fact it does not have the geometry characteristic of these systems. Furthermore, its polyhedron can be regarded as a three-cap trigonal prism [with the C(3)B(5)B(9) and B(4)B(7)B(10) bases and the Fe(1), Fe(6), and B(8) "caps"] having one additional vertex at C(2), which corresponds to 9-vertex *closo*-MCB (20 electrons).

A number of interesting 10-vertex MCB and metalloborane complexes have been described by Crook and co-workers,[47–50] who investigated the reactions of the iridium complex *trans*-$[Ir(CO)Cl(PPh_3)_2]$ with the *closo*-$B_{10}H_{10}^{2-}$ borate dianion in

#According to the IUPAC nomenclature, the term *commo*-MCB is given to complexes in which the polyhedra are linked together via a common metal atom.

methanol. In the course of the formation of two of the products investigated, namely $(MeCOO)(Ph_3P)HIrCB_8H_7 \cdot (PPh_2)$[47] and $IrC(OH)B_8H_6(OMe)(C_6H_4PPh_2)(PPh_3)$[48] (Fig. 8), a carbon atom from the solvent as well as the metal atom was inserted in the borane skeleton during the reaction, which resulted in the formation of 10-vertex iridacarbaboranes. The first of these complexes has 22 skeletal electrons (in calculating the number of electrons one must take into account the Zwitter-ionic character of the molecule—the positive charge of the P atom linked to the B atom and the negative charge on the polyhedral skeleton) and possesses the geometry of a fairly symmetrical (the Ir^{III} atom has the d^6 configuration) two-cap square antiprism, which is characteristic of 10-vertex *closo*-MCB.

The second complex investigated contains two skeletal electrons less, because, firstly, it has no hydride ligand and, secondly, its polyhedron does not carry a negative charge. The Ir(7)...B(9) distance in this complex is fairly large (2.82 Å) and the authors[48] characterised it as a *nido*-MCB and the Ir(7)B(8)B(9)C(10) face is regarded as open. Furthermore, the similarity of the polyhedra of this iridacarbaborane and the bimetallic iron complex discussed above is striking. The similarity appears entirely reasonable because both complexes are, as it were, "superelectron-deficient" (see above) 10-vertex classical systems and each has 20 skeletal electrons. As in the iron derivative, in the polyhedron of the iridium complex there is one "additional" vertex, which in this instance is occupied by the B(3) boron atom. It must also be emphasised that the purely boron hydride complex $(Ph_3P)(Ph_2PC_6H_4)HIrB_9H_8$, obtained by the reaction of $IrCl(PPh_3)_3$ with $B_9H_{12}^-$, which is isoelectronic with the above compounds, has an analogous structure, which has been characterised[49] (Fig. 8).

The reaction involving the formation of iridium complexes, mentioned above, has an interesting feature: in these processes the *ortho*-boration of one of the benzene rings of the Ph_3P ligand takes place simultaneously with the insertion of the metal atom in the borane polyhedron. It has been found that similar processes play an important role in the chemistry of MCB and metalloboranes containing triphenylphosphine ligands. Thus, apart from the products mentioned above, the octahedra of the metalloborane $(OC)_3(Ph_3P) \cdot (Ph_2PC_6H_4)_2Ir_2B_4H_2$,[50] in which the metal atoms occupy two neighbouring vertices, have been isolated and structurally characterised in the reaction of $Ir(CO)Cl(PPh_3)_2$ with *closo*-$B_{10}H_{10}^{2-}$, apart from the products mentioned above. Here the benzene rings of the two phosphine ligands at one of the metal atoms have undergone *ortho*-boration. The authors[49,50] suggest that the *ortho*-boration process is not simply a concomitant reaction, involving the elimination of hydrogen atoms in the formation of C–B bonds in the polyhedral skeleton already present, but constitutes an important stage involving the insertion of the metal atom into the polyhedron. In their view the CH group in the benzene ring can serve during the reaction as a source of an additional electron pair, which is supplied to the borane polyhedron and initiates its decomposition.

Incidentally, this view can be open to a definite objection, particularly if one takes into account the results obtained in a structural study[51] of the products of the thermal rearrangement of the 10-vertex *nido*-platinacarbaborane $(Ph_3P)_2 \cdot Pt(CB_8H_{12})$ discussed above (Fig. 6). When this complex is heated, two moles of H_2 are evolved and bonds are formed between the *ortho*-carbon atoms of two benzene rings in different Ph_3P groups and the boron atoms in the 8- and 10-positions.

Thus the *ortho*-boration of the benzene rings of the triphenylphosphine ligands need not necessarily be accompanied by rearrangements in the polyhedral skeleton. It may be that the specific features of the reaction are associated with the enforced geometrical proximity in the C–H (benzene ring) and B–H (carbaborane ligand) bonds, which are characterised by the opposite polarisations of the hydrogen atoms.

4. 9-Vertex MCB

As a rule, 9-vertex MCB consist of a polyhedron having the form of a three-cap trigonal prism. Such geometry is characteristic of, for example, the MCB anion $[CpCoCB_7H_8]^-$, whose structure has been investigated[52] using its caesium salt (Fig. 9). Here the carbon atom occupies a low-coordination position in one of the "caps", while the cobalt atom is located at one of the vertices of the base. The differences between the Co–B(5) and Co–B(6) distances (on average

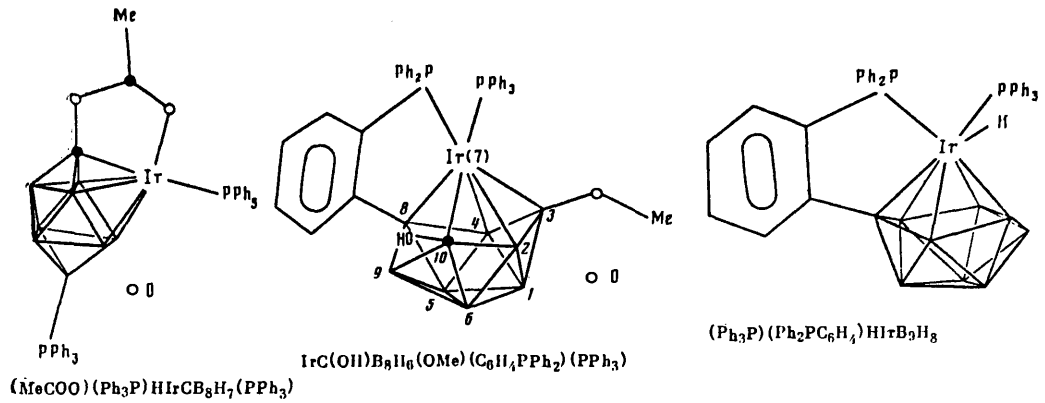
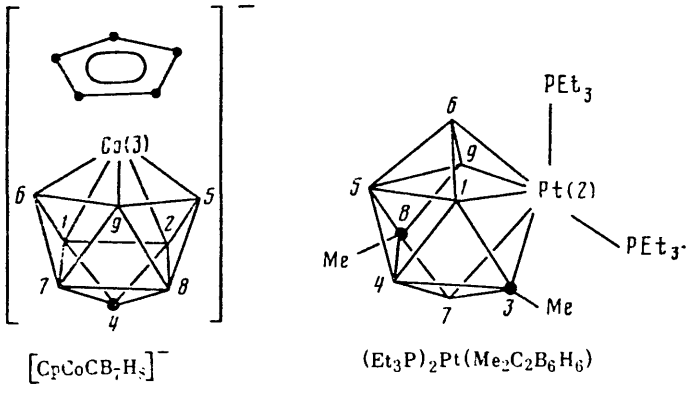


Figure 8. Borane and carbaborane complexes of iridium.[47–49]

1.98 Å) and between the Co–B(1), Co–B(2), and Co–B(9) distances (on average 2.16 Å) can be explained by the lower C.N. of the B(5) and B(6) atoms in the "caps" of the polyhedron.



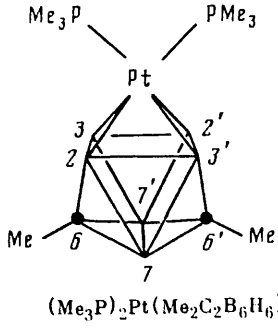


Figure 9. 9-Vertex MCB.[52–54]

Two 9-vertex platinacarbaboranes with analogous compositions, namely $(Et_3P)_2Pt(Me_2C_2B_6H_6)$[53] and $(Me_3P)_2.Pt(Me_2C_2B_6H_6)$,[54] have appreciably different structures. In the first compound, where the platinum atom occupies one of the vertices in the base of the prism, as in the platinum(II) complexes discussed above, appreciable distortions of the polyhedron are observed: the platinum atom forms two short Pt(2)–B(6) (2.17 Å) and Pt(2)–C(3) (2.18 Å) bonds (which, together with the PEt_3 ligands, build up its environment to a square) and three long bonds with the boron atoms in the 1-, 7-, and 9-positions having an average length of 2.48 Å. The B(7)...B(9) distance in the base of the prism does not correspond to the formation of a bond and the Pt(2)B(7)C(8).B(9) face is "open".

On the other hand, the polyhedron ot the triphenylphosphine derivative of platinum is actually symmetrical: four Pt–B bonds are 2.19–2.24 Å long. Thus this complex infringes the rule, mentioned above, concerning the appearance of appreciable distortions in the polyhedron following the introduction of an atom with a d^8 configuration. The only anomaly in the structure consists, in this instance only, in the location of the metal atom at a low-coordination vertex of the polyhedron.

5. 8-Vertex MCB

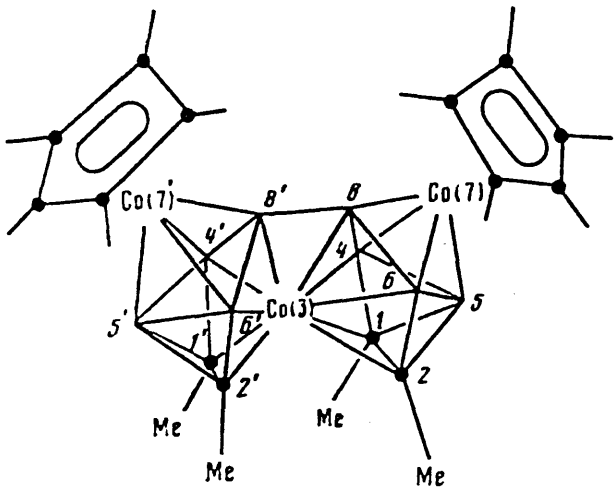
The 8-vertex *closo*-MCB should have the structure of a dodecahedron with triangular faces according to the general scheme (Table 2). This very interesting polyhedron can be regarded as a combination of two distorted tetrahedra (it is sometimes referred to as a "Siamese" polyhedron. Indeed, in order to obtain this polyhedron, it is necessary to extend one tetrahedron and to compress the other along the $\bar{4}$ symmetry axis and then insert one in the other.

In the cobaltacarbaborane $(C_5Me_5)_2Co_3Me_4C_4B_8H_7$ [55] the two dodecahedral fragments are combined not only via the carbon metal atom in a *commo*-type arrangement but also via a B–B bond 1.758 Å long, which is exopolyhedral in relation to both MCB skeletons (Fig. 10). Both crystallographically independent dodecahedra have virtually identical geometries and a fairly symmetrical structure: the breakdowns in symmetry are evidently associated with the different radii and C.N. of the atoms forming part of the polyhedron. The molecule as a whole has an approximate symmetry plane perpendicular to the B(8)–B(8′) bond. The absence of a second possible mirror plane is associated with the small but significant rotation of the dodecahedral fragments relative to one another as a result of which the C(1)...C(1′) distance is shorter by approximately 0.1 Å than the C(2)...C(2′) distance. This rotation has been attributed[55] to the influence of the additional H atom [apart from the terminal H atoms at the B(4), B(5), and B(6) atoms], which was not detected in the structural study and which is apparently located in the vicinity of the Co(3), B(6), B(8), B(6′), and B(8′) atoms.

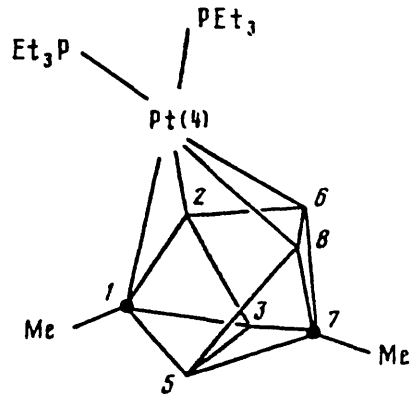
The only 8-vertex MCB with an isolated polyhedron, whose structure has been investigated hitherto, namely $(Et_3P)_2.Pt(Me_2C_2B_5H_5)$,[56] is a platinum(II) derivative and its polyhedron is highly distorted as was to be expected. The coordination of the platinum atom can be regarded as of the "square-planar" type [involving the P atoms in the centres of the B(2)–B(6) and B(6)–B(8) edges]. On the other hand, the formation of a bond along any of the two diagonals of the "open" Pt(4)C(1)B(5)B(8) face [Pt(4)...B(5) = 3.105 Å; C(1)...B(8) = 2.896 Å] would have led to a *closo*-dodecahedral structure.

Although the number of structural studies of 8-vertex MCB has been extremely small, the dodecahedral borate dianion $B_8H_8^{2-}$ has been known for a fairly long time.[57] The dodecahedral metalloboranes $Cp_4Co_4B_4H_4$ [58] and $Cp_4Ni_4B_4H_4$ [59] have been obtained recently and their structures characterised (Fig. 10). These compounds are interesting because they have a symmetrical *closo*-structure, although the former has two electrons less and the latter two electrons more than required by Wade's rule. It is natural therefore that the studies of these structures were immediately followed by a whole series of theoretical investigations in which attempts were made to account for the causes responsible for the breakdown of the "2n + 2" rule for the dodecahedron.

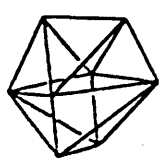
It has been noted in the study of Wade and co-workers[60] that the HOMO and the LUMO of the cluster system having the dodecahedral structure are non-degenerate, in contrast to the frontier orbitals of almost all the remaining *closo*-polyhedra. Therefore, although the introduction of two additional electrons into the dodecahedral system or conversely the removal of an electron pair leads to some loosening of the bond in the polyhedron, nevertheless it does not cause appreciable distortions in the latter. On the other hand, a change in the number of skeletal electron pairs in the majority of other *closo*-systems with degenerate frontier orbitals would have led to the appearance of an unstable paramagentic complex, which is distorted as a consequence of the Jahn–Teller effect. This qualitative study has been



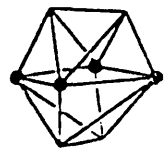
$(C_5Me_5)_2Co_3Me_4C_4B_8H_7$



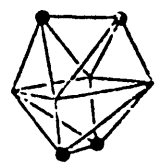
$(Et_3P)_2Pt(Me_2C_2B_5H_5)$



$B_8H_8^{2-}$



$Cp_4Co_4B_4H_4$



$Cp_4Ni_4B_4H_4$

Figure 10. MCB and metalloboranes with 8-vertex polyhedra.[55-59]

confirmed by quantum-chemical calculations for dodecahedral borane and metalloborane systems by the extended Hückel method.[61] The calculation not only justified the stability of the dodecahedral systems not satisfying Wade's rule but also made it possible to explain why the metal atoms in the nickel dodecahedron with an "electron excess" occupy the vertices of an extended tetrahedron or why those in the cobalt complex with an "electron deficiency" are located at the vertices of a compressed tetrahedron.

6. Small (7- and 6-Vertex) MCB

Among the small MCB, the compounds with a 7-vertex polyhedron, having the geometry of a pentagonal bipyramid have been studied in greatest detail. The metal atom in such polyhedra usually occupies a high coordination apical site, as happens, for example in the cobaltacarbaborane $CpCo(Me_2C_2B_4H_4)$[62] (Fig.11), which can serve as an example of a complex with a symmetrical structure typical for 7-vertex MCB. The cobalt atom is located at the high-coordination apical site and is linked symmetrically to the atoms in the equatorial plane (Co–C = 2.031 Å; Co–B = 2.092 Å); the carbon atoms occupy the neighbouring vertices in this plane and the length of the C–C bond (1.461 Å) is close to that found in the dodecahedral fragments of the cobaltacarbaborane $(C_5Me_5)_2Co_3Me_4C_4B_8H_7$ (on average 1.448 Å[55]), mentioned above, and are much shorter than in the analogous eicosahedral systems. This difference is evidently associated with the differences between the C.N. of the carbon atoms in the dodecahedron and the pentagonal bipyramid (C.N. = 4), on the one hand, and in the eicosahedron (C.N. = 5), on the other.

Having examined the structure of a symmetrical cobaltacarbaborane (with the d^6 configuration), we shall now turn to the discussion of the structure of the analogous platinum(II) derivative (with the d^8 configuration). As in all the derivatives of d^8 metals examined above, significant distortions of the geometry of the polyhedron were observed in this instance. The distortions in the 7-vertex MCB have the character of a "shift" deformation analogous to those observed for the eicosahedral MCB. Thus the platinum atom in the complex $(Et_3P)_2Pt(Me_2C_2B_4H_6)$[63] is much closer to the boron atoms (the average Pt–B distance is 2.21 Å) than for the carbon atoms (the average Pt–C distance is 2.855 Å); the angle of inflection of the "open" face along the B...B line,

which tends to shift the carbon atoms away from the metal atom, is 21.4° [in the corresponding 12-vertex complex $(Et_3P)_2PtC_2B_9H_{11}$ [28] the average Pt...C distance is 2.572 Å and the ange of inflection of the "open" face is 9.1°].

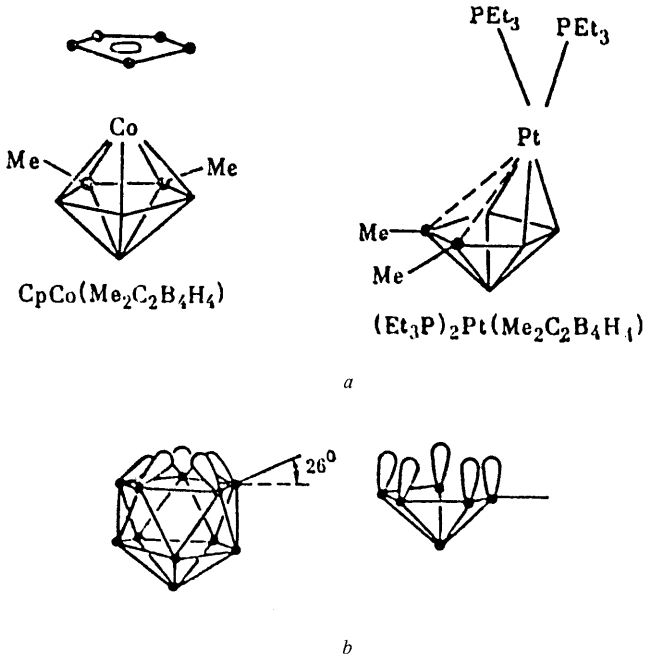


Figure 11. *a*) 7-Vertex MCB;[62,63] *b*) the orientation of the "lobes" of the frontier orbitals of *nido*-carbaborane ligands.[64]

Comparison of these geometrical parameters shows that, although the "shift" distortions in the 7- and 12-vertex polyhedra are of the same type, in the case of the small MCB they are more distinct. This difference is linked directly to the different directions of the exopolyhedral bond in the eicosahedron and in the pentagonal bipyramid. Indeed, in the eicosahedron the exopolyhedral bond emerges from the plane of the pentagonal face in the direction of the vertex centred above it (the angle between the direction of this bond and the plane of the face is 26°), while in the pentagonal bipyramid the exopolyhderal bond is in the equatorial plane. Calculations by the extended Hückel method[64] have shown that this difference leads to different orientations of the "lobes" of the frontier orbitals of the carbaborane ligand: in the eicosahedral fragment the long axes of the "lobes" form a much smaller angle with the plane of the "open" face than in the pentagonal bipyramidal fragment (Fig.11). Bearing in mind that the "shift" distortions in the coordination of the dicarbollide ligand are caused by the preferential localisation of the frontier orbitals at the boron atoms, it becomes understandable why the different orientation of the "lobes" of the orbitals in the pentagonal bipyramid requires a more significant shift of the metal atom in the direction of the boron atoms to achieve a more effective overlap. Such orientation in the orbitals also explains the weaker bonding of the metal atom in the 7-vertex polyhedra compared with the 12-vertex polyhedra, which leads to different barriers to the rotation of the PtP_2 fragment relative to the carbaborane ligand.

Thus two singlets are observed in the ^{31}P NMR spectrum of the platinum dicarbollide complex even at room temperature, while in the spectrum of the pentagonal bipyramidal complex this splitting of the signal is observed only when the temperature is reduced.[63]

A whole series of structural studies on 7-vertex MCB have been undertaken to investigate the unusual chemical properties of derivatives of their hydride *commo*-MCB $(Me_2C_2B_4H_4)_2FeH_2$ (Fig.12). The hydride hydrogen atoms could not be located in a study[65] of the structure of the initial complex. These atoms are apparently disordered and are alternately centred above the four FeB_2 faces of the two pentagonal bipyramidal polyhedra. The presence of the hydrogen atoms is responsible for the appreciable mutual inclination of the pentagonal faces (the dihedral angle is 7.8°), which leads to the appearance of the energetically unfavourable short intramolecular contact Me...Me = 3.53 Å.

Each polyhedron of the complex $(Me_2C_2B_4H_4)_2FeH_2$ contains $2n + 2$ skeletal electrons and satisfies Wade's rule. This can be readily demonstrated by taking into account the fact that the "neutral" carbaborane ligand $Me_2C_2B_4H_4$ serves as a donor of four electrons, while the hydride hydrogen atoms can be regarded, for simplicity, as bound only to the metal atom (in this case the iron atom contributes two electrons to the polyhedron).

For an alternative description of the bonding in the complex under discussion, one can resort, as in the case of other MCB systems with giant polyhedra, to the topological model of a superaromatic cluster proposed by Slovokhotov and Struchkov.[66] In this model the total number of skeletal electrons and the number of vertices in both giant polyhedra are evaluated and the atoms belonging to the two skeletons are taken into account only in the determination of the number of electrons and are not included in the total number of vertices. In the *commo*-complex considered each MCB group serves as a rule as a donor of two electrons and the MCB groups each contribute three electrons to the polyhedron; on the other hand, the presence of the iron atom in this system leads in essence to a decrease of the number of skeletal electrons (the contribution of the iron atom is $8 + 2 - 12 = -2$). Thus the total number of electrons in the complex $(Me_2C_2B_4H_4)_2FeH_2$ is 26, which corresponds to 12 (without taking into account the iron atom) vertices of the polyhedron.

The specific features of the chemical behaviour of the complex $(Me_2C_2B_4H_4)_2FeH_2$ are associated with its ability to lose readily the hydride hydrogen atoms and to combine with metal-containing groups. This result in the formation of compounds in the molecules of which two carbaborane ligands are combined not only via the common central metal atom but also via yet another, additional atom occupying the position of a "cap" in relation to one of the triangular faces in each polyhedron. Such compounds can be called "wedged" *commo*-MCB.

Thus the interaction of the initial iron hydride complex with $CpCo(CO)_2$ and $Co(PEt_3)_4$ leads to the formation of mixed bimetallic MCB having the compositions $CpCoFe(Me_4C_4B_8H_8)$[67] and $(Et_3P)_2CoFe(Me_4C_4B_8H_8)$,[68] which have been investigated by X-ray diffraction. In the study of the electronic structures of these compounds it is convenient to employ the topological model of joined polyhedral systems.[66] In the cyclopentadienylcobalt complex, which incorporates, apart from the CpCo group, four CMe groups, eight BH groups, and the iron atom, there are 26 electrons corresponding to 12 "outer" (disregarding the iron atom and the "additional" BH group) vertices of the joined polyhedron. As a consequence of the replacement of the Cp ligand in the phosphine complex by two Et_3P groups, the number of skeletal electrons

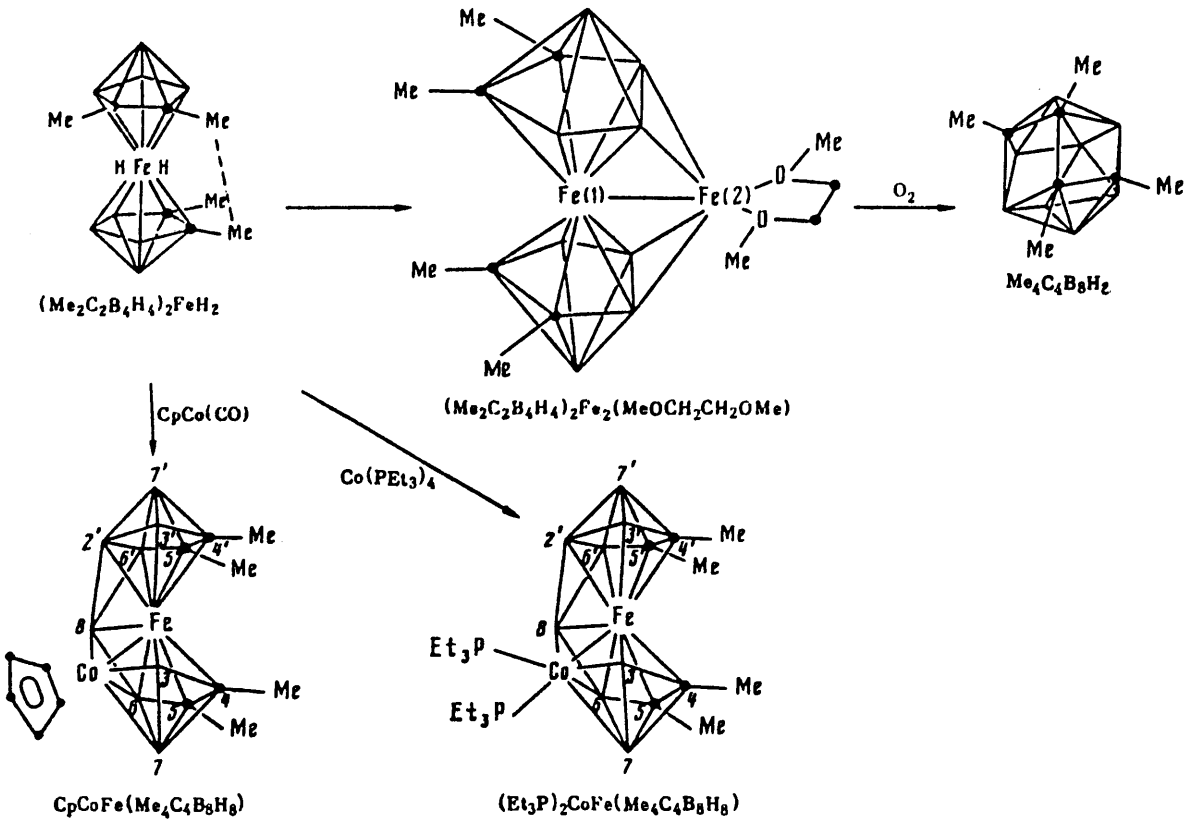


Figure 12. The structure of $(Me_2C_2B_4H_4)_2FeH_2$ and its reaction products.[65,67,68,71,72]

should be one less. This difference in the atomic structure influences in the given instance also the geometrical characteristics: almost all the bonds involving the cobalt atom and the boron atom located at the "additional" vertex in the phosphine complex are longer (on average by 0.08–0.10 Å) than the corresponding distances in the cyclopentadienyl derivative.

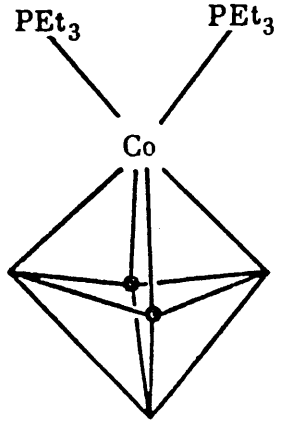
This explanation of the difference between bond lengths in the complexes described appears somewhat more correct than the remark by Barket et al[68] concerning the difference between the polyhedral radii of the cobalt(II) (in the Et_3P complex) and cobalt(III) (in the Cp derivative) atoms. Naturally the "deficit" of electron density (−1e) in such cluster systems is not localised solely at the metal atom but is distributed to a greater or lesser degree throughout the polyhedron. Precisely as a consequence of such delocalisation, not only the bond involving the Co atom but also others (for example, the edges connecting the additional BH group to the Fe and B atoms) are lengthened in the polyhedron of the phosphine complex.

An interesting feature of the iron and cobalt complexes is the asymmetric disposition of the "additional" BH group relative to the coordination planes of the carbaborane and MCB ligands, which is expressed by greatly increased (by approximately 0.3 Å) B(8)–B(2′) and B(8)–B(6′) distances compared with the B(8)–B(6) bond. This provided the authors[69] with a basis for the hypothesis that the "additional" BH group is linked only to the polyhedron containing the cobalt atom and that the relatively short distances to the boron atoms in the other polyhedral fragment are determined solely by the geometrical requirements—the repulsion of the Me groups to the "opposite" side of the polyhedron. In this case the "wedged" complexes can be represented as the usual *commo* MCB in which the 7- and 8-vertex polyhedra are combined via the common iron atom.

However, this view was disproved in a study[70] where a quantum-chemical calculation was carried out on the "wedged" metalloboranes and MCB by the extended Hückel method. The calculations showed that in the model borate anion $[Fe(BH)(B_6H_6)_2]^{4-}$ a symmetrical disposition of the "additional" boron atom relative to the coordinating faces of the *nido*-borane ligands corresponds to an energy minimum and the overlap of the frontier orbitals of each ligand with those of the "additional" BH group is equally important for the bonding in the polyhedron. It has been shown by the methods of perturbation theory that the introduction of the CoCp group instead of one of the BH groups of the borane ligand alters the character of the frontier orbitals of this ligand, which creates more favourable conditions for the overlap with the orbitals of the "additional" BH group. However, such substitution cannot lead to the complete dissociation of the bond between this group and the second, frequently borane, fragment.

The structure of a MCB of the "wedged" type, which constitutes an intermediate in the "oxidative cross-linking" of the ligands in the initial hydride complex $(Me_4C_2B_4H_4)_2FeH_2$, has also been investigated (Fig.12). This process, which proceeds readily in the presence of oxidants and leads to the formation of the tetracarbon carbaborane $Me_2C_4B_8H_8$, has been studied in detail.[71,72] The investigation of mixtures of the complexes $(R_2C_2B_4H_4)_2FeH_2$ with various alkyl radicals R

established that the "cross-linking" of the carbaborane groups does not entail the intermolecular exchange of ligands. In the presence of oxygen or rather oxidants, the "cross-linking" process in the tetrahydrofuran or dimethoxyethane solutions of the hydride complexes takes place almost instantaneously. However, in an inert atmosphere these solutions can persist for a short time (several hours) and the colour changes from dark-red to violet only gradually. The introduction of even trace amounts of oxidants into such a solution induces the instantaneous formation of the tetracarbon carbaborane $R_4C_4B_8H_8$.



$(Et_3P)_2CoC_2B_3H_5$

Figure 13. The structure of $(Et_3P)_2CoC_2B_3H_5$.[77]

The crystals of the intermediate in the "cross-linking" process isolated from the violet solution proved, however, to be fairly stable in air and were investigated by X-ray diffraction.[72] It was found that the molecule of the bimetallic complex $(Me_2C_2B_4H_4)_2Fe_2(MeOCH_2CH_2OMe)$ (Fig.12) contains one of the iron atoms at the "additional" vertex of the "wedged" *commo*-MCB. In contrast to the compounds examined above, the "additional" vertex in this complex [the Fe(2) atom] is located symmetrically relative to the two identical carbaborane ligands. Although the Fe(1)–Fe(2) distance in this structure (2.414 Å) is appreciably smaller than the lengths of the analogous bonds in the other MCB polyhedra (see above, for example), the authors[72] conclude that there is no direct Fe–Fe interaction on the basis of the results of magnetic measurements and the EPR spectra of this paramagnetic complex. Bearing in mind the short Fe–Fe distance, this conclusion appears to us extremely controversial. Thus the electronic structure of this unusual complex, which does not satisfy any of the rules for the evaluation of the number of skeletal electrons employed above, is not as yet entirely clear.

In conclusion of the discussion of the 7-vertex MCB, we may mention bimetallic monopolyhedral pentagonal-bipyramidal complexes. Such compounds, for example, the cobaltacarborane $Cp_2Co_2MeC_2B_3H_4$,[73] can be regarded, on the one hand, as the usual *closo*-MCB systems satisfying the "$2n + 2$" rule and, on the other hand, they can be formally treated as "three-decker" sandwiches made up of the Co^{3+} cations and the $C_5H_5^-$ and $C_2B_3H_5^{4-}$ anions, because these molecules contain a planar carborane face to which two metal atoms are coordinated simultaneously. Although this treatment proved to be extremely useful and stimulated to a considerable extent very interesting studies on the synthesis[74,75] of "multidecker" systems as well as their theoretical investigation,[76] the cluster model of delocalised interactions is undoubtedly more important for the description of the nature of the bonding in MCB of this kind. This is indicated, in particular, also by the stability of such complexes, which distinguishes them from the unstable purely cyclopentadienyl "multidecker" derivatives.

The results of the first structural investigation of the 6-vertex octahedral MCB complex $(Et_3P)_2CoC_2B_3H_5$ were not published until 1980.[77] This complex (Fig.13) belongs to the class of the paramagnetic *closo*-MCB, mentioned above, which contain one skeletal electron less than is required by the "$2n + 2$" rule. As mentioned above, it is as yet not entirely clear how this anomaly in the electronic structure influences the geometry of the polyhedron. One can only note that appreciable differences between the Co–C (2.112 Å) and Co–B (1.955 Å) distances as well as appreciable deviations from planarity in the equatorial belt of the octahedron (the angle of inflection along the B...B line is 19°) are observed in the given structure

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In a brief review, it is naturally impossible to dwell on a whole series of other aspects of the structural chemistry of the MCB. We disregarded many structures of *closo*- and *nido*-MCB, did not consider at all complexes with the *arachno*-structure, and did not discuss the extensive class of tetracarbon MCB, which is being vigorously investigated. All these questions undoubtedly merit additional consideration. Here we concentrated attention on compounds with *closo*-polyhedra containing between six and twelve vertices.

In conclusion of the discussion of these compounds, it must be emphasised yet again that the entire wide variety of these structures can be classified and interpreted on the basis of the rules for the counting of skeletal electrons widely employed in cluster chemistry. The overall geometry of the MCB molecules obeys these rules fairly rigorously.

On the other hand, small and sometimes also not very small distortions in the geometry of the polyhedra depend to a large extent on the nature of the metal and primarily on its electronic configuration. Thus, as the *d* sublevels of the metal atoms in the series of transition and post-transition elements are filled, geometrical distortions arise in the MCB systems and become increasingly more marked, being expressed by a decrease of symmetry and a loosening of the polyhedron. Analysis[78] of structural data on the cyclopentadienyl derivatives of post-transition elements has shown that this trend, namely the enhancement of coordination distortions as the *d* sublevels of the metal atoms are filled, is extremely general: it is manifested in complexes of transition and post-transition elements with both planar aromatic and polyhedral "superaromatic" ligands.

Yet another comment may be made on this subject. In all the MCB complexes of bivalent platinum mentioned above, the distortions of the polyhedron lead to a disposition of the strongest bonds involving the metal atom which imitates the square planar coordination characteristic of the usual classical platinum(II) complexes. In considering this question in a wider sense, one may stress that symmetrical MCB *closo*-polyhedra are observed only for metals with the electronic configuration for which an octahedral environment is typical (Fe^{II}, Fe^{III}, Co^{III}, Pt^{IV}, etc.). The introduction into the

carbaborane polyhedron of metals having a less symmetrical coordination [tetragonally distorted octahedral (Cu^{II}), square planar (Pt^{II}, Pd^{II}), and linear (Hg^{II})] leads as a rule to a considerable loosening and (or) decrease of the symmetry of the polyhedron.

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Advances in the Study of the Mechanism of the Gas-phase Oxidation of Aldehydes

I.A.Vardanyan and A.B.Nalbandyan

The results of studies of the kinetics and mechanism of the gas-phase oxidation of aliphatic aldehydes are examined in relation to CH_2O, CH_3CHO, and C_2H_5CHO, which are intermediates in the oxidation of hydrocarbons and the general rules governing the course of these degenerate-branched chain processes are established. Attention has been concentrated on the role of heterogeneous factors. It is shown that heterogeneous chain branching as a consequence of the radical decomposition of CH_3CO_3H or $C_2H_5CO_3H$ takes place in the low-temperature oxidation of acetaldehyde and propionaldehyde; the experimental data on the heterogeneous radical decomposition of organic peroxy-compounds are considered.
The bibliography includes 163 references.

CONTENTS

I.	Introduction	532
II.	Characteristic features of the kinetics of the oxidation of aldehydes	532
III.	The role of heterogeneous factors in the oxidation of aldehydes	535
IV.	The negative temperature coefficient of the maximum rate of reaction	539
V.	Conclusion	540

I. INTRODUCTION

Aldehydes are the main intermediates in the oxidation of hydrocarbons and the study of the mechanisms of their oxidation can help in determining such mechanisms. The characteristic features of the oxidation of aldehydes are described satisfactorily from the standpoint of the concept of degenerate branched chain reactions.[1-9] The determination of the true mechanism of these processes constitutes an important stage in the further development of the theory of chain reactions and also in the development of the scientific principles of the direct preparation of the compounds involved such as peroxyacids, acids, hydrogen peroxide, etc. which are widely used in various branches of the national economy.

Recent studies of the dependence of the kinetics of the oxidation of CH_3CHO and C_2H_5CHO on the nature of the surface of the reaction vessel over a wide temperature range revealed a number of unusual features.[10-14] This led to the revision of the ideas concerning the character of certain elementary stages, in particular the chain branching stage.

One of the important problems in the kinetics of the gas-phase oxidation reactions involves the elucidation of the causes of the appreciable rate of oxidation of acetaldehyde and propionaldehyde at temperatures below 473 K down to room temperature and the inertness of formaldehyde at these temperatures,[13,14] although the C–H bond energies in the CHO groups of the above compounds are identical.

The negative temperature coefficient (NTC) of the maximum rate of oxidation of aldehydes (CH_3CHO and C_2H_5CHO) observed comparatively recently,[15,16] stimulated studies whose aim was to elucidate the causes of the appearance of this coefficient both in the case of aldehydes and hydrocarbons.

The present state of the experimental and theoretical investigations is analysed in the present review in relation to the oxidation reactions of CH_2O, CH_3CHO, and C_2H_5CHO and the development of ideas concerning the mechanism of these reactions, particularly from the standpoint of allowance for the role of heterogeneous factors, is traced. The characteristic features and the general rules governing these processes have been elucidated and an approach to the development of a method for the selective gas-phase oxidation of aldehydes to acids and peroxyacids by appropriate treatment of the surface of the reaction vessel (treatment with a particular substance) or by altering the surface to volume (S/V) ratio has been formulated on their basis.

II. CHARACTERISTIC FEATURES OF THE KINETICS OF THE OXIDATION OF ALDEHYDES

The oxidation reactions of formaldehyde and acetaldehyde have now been investigated in detail. The conclusions reached have been extended to propionaldehyde, which is legitimate in view of the experimental demonstration of common features[5] of the oxidation of CH_3CHO and C_2H_5CHO. The principal results of the kinetic studies for formaldehyde have been discussed in review articles[6-9] and in a communication.[17] Studies devoted to acetaldehyde and propionaldehyde have been described in Refs.5–9 and 18–25 and Refs.5–9, 12, 14, 26, and 27 respectively.

The principal result of these investigations, common to all the aldehydes, is that the reactions proceed via a degenerate branched chain mechanism with autoacceleration. It has been shown for the photochemical oxidation of acetaldehyde and propionaldehyde that the chains in these reactions are long (~1000 units).[28-31] The chain character of the process is indicated also by the inhibition of the reaction by the addition of small amounts of a number of compounds.[32-35] The chain mechanism of the reaction involving formaldehyde has been demonstrated by the decreased rate of the process with increase of the S/V ratio.[36]

The product responsible for chain branching is a peroxy-compound—hydrogen peroxide in the high-temperature oxidation of formaldehyde and a peroxyacid in the oxidation of acetaldehyde and propionaldehyde. This conclusion is based on the acceleration of the reaction following the addition of RCO_3H [37-40] and also by the results of experiments[5] using the "quenching" method. After rapid cooling to 298 K, the acetaldehyde–oxygen mixture which has partly reacted at 488 K ignites spontaneously at a lower temperature on reheating. A similar phenomenon has been observed also for synthetic $CH_3CHO + O_2$ mixtures with added peroxyacetic acid. The degenerate chain branching has been attributed[5] to peroxyacetic acid and its existence in two forms has been

suggested—more and less stable forms, the former being partly converted into the latter during quenching.

The chain branching stage was initially attributed to the reactions of the peroxyacid, namely the decomposition of the peroxy-complex [$RCO_3H.RCHO$][8,27,39,41,42] or the homogeneous decomposition of RCO_3H.[32,33,43,44] The formation of a peroxy-complex was claimed on the basis of the inconsistency observed in a number of instances between the decrease of pressure in the system and the pressure of the RCO_3H formed, which was particularly clearly manifested at $T <$ 353 K.[39] The only criterion of the occurrence of the branching stage with participation of the peroxy-complex below 423 K is believed to be[39] the dependence of the maximum rate of the oxidation reaction on the square of the aldehyde concentration, which follows from the mechanism adopted (on the assumption of long chains and the neglect of the rate of initiation in mixtures with a high aldehyde content):

$$RCHO + O_2 \rightarrow R\dot{C}O + H\dot{O}_2,$$
$$R\dot{C}O + O_2 \rightarrow RC\dot{O}_3,$$
$$RC\dot{O}_3 + RCHO \rightarrow RCO_3H + R\dot{C}O$$
$$\left.\begin{array}{l} 2R\dot{C}O \rightarrow \\ R\dot{C}O + RC\dot{O}_3 \rightarrow \\ 2RC\dot{O}_3 \rightarrow \end{array}\right\} \text{chain termination},$$
$$RCO_3H \rightarrow RC\dot{O}_2 + \dot{O}H$$
$$RCO_3H + RCHO \rightarrow \text{radicals},$$
$$R = CH_3,\ C_2H_5.$$

It has been stated[45] that the maximum rate calculated from the $p-t$ curves (p is the pressure and t the time) cannot serve as criterion of the correctness of the choice of a particular branching reaction in view of the low accuracy of its determination.

The hypothesis that a peroxy-complex is formed in a gas phase with subsequent decomposition into radicals in space or on the reactor surface is relatively unjustified and has been put forward mainly by analogy with the situation observed in the liquid-phase oxidation.[46] A number of studies have been devoted to the question of the existence of the peroxy-complex in the gas phase.[47-50] Solely on the basis of the iodometric analysis of the reaction products, the formation of the aldehydomonoperacetate (AMP) via the following pathway has been claimed:

$$CH_3CHO + CH_3CO_3H \rightarrow CH_3-\underset{\displaystyle OO}{\overset{\displaystyle OH}{C}}-H \quad \overset{\displaystyle O}{C}-CH_3.$$

AMP then decomposes:

$$AMP \rightarrow \begin{cases} \rightarrow CH_3CHO + CH_3CO_3H; \\ \rightarrow 2CH_3CO_2H. \end{cases}$$

In contrast to the liquid-phase acetaldehyde oxidation reaction, in which the presence of an adduct has been confirmed by NMR,[51,52] no such convincing evidence is available for the gas-phase process.

As regards the homogeneous decomposition of RCO_3H its contribution to the branching process at temperatures up to 473 K is low owing to the high activation energy[53-55] and it is difficult to account for the higher rates of oxidation of CH_3CHO at low temperatures by its formation.

The involvement of hydrogen peroxide in chain branching in the high-temperature oxidation of formaldehyde has been demonstrated[56] by the disappearance of the induction period following the addition of the maximum amount of H_2O_2 observed in the course of the reaction.

There has been no unanimous view concerning the mechanism of the low-temperature oxidation. The nature of the peroxy-compounds, i.e. H_2O_2[7,57,58] or HCOOOH,[4,8,59,60] has been the subject of controversy for a long time. This uncertainty was caused, on the one hand, by the deficiencies of the method of iodometric analysis used by the authors, which failed to yield an unambiguous answer and has been criticised at one time,[3] and, on the other hand, by the possibility of the formation of an organic peroxide, in particular dioxymethyl peroxide, on interaction of CH_2O with H_2O_2 outside the reaction zone.[61]

The formation of HCO_3H has been postulated[60] solely on the basis of the presence of peaks corresponding to masses of 60, 61, and 62 in the mass spectrum of the CH_2O oxidation products, which is unjustified without a comparison with the mass spectrum of the authentic compound. A recent communication[62] quotes the mass spectrum of HCO_3H and presents a comparison with the results of the mass-spectrometric analysis of the products of the low-temperature oxidation of formaldehyde and a mixture containing CH_2O and H_2O_2. In the last two stages the spectra hardly differed. On this basis, it was concluded that the presence of peaks with m/e 60–62 in the analysis of the formaldehyde oxidation products is associated with the products of the interaction of CH_2O and H_2O_2 outside the reaction zone and not with the presence of HCO_3H.

The absence of HCO_3H from the low-temperature formaldehyde oxidation products in a reactor treated with boric acid has been established by analysing the organic peroxyacid in the presence of H_2O_2 using a photoelectric colorimeter (PEC) with the aid of benzidine[63] and *o*-toluidine[64] hydrochlorides. The kinetics of the consumption of CH_2O and the accumulation of H_2O_2 have shown that the chain branching in the low-temperature oxidation of CH_2O is caused by the bimolecular homogeneous decomposition of H_2O_2 into two $\dot{O}H$ radicals.[17]

An important factor in the determination of the mechanism of a chain reaction is the elucidation of the nature of the chain propagating active centre. Progress in this direction has been associated with the employment in the investigations of the kinetic method involving the freezing out of the radicals combined with EPR spectroscopy.[65]

According to published data, the chain propagating active centres in the oxidation of aldehydes are the peroxy-radicals $RC\dot{O}_3$ for acetaldehyde and propionaldehyde and $H\dot{O}_2$ for CH_2O. This conclusion has been based on the presence of acetyl peroxide in the products of the photochemical oxidation of acetaldehyde[66] and also the direct detection of peroxy-radicals by EPR in the thermal oxidation of CH_3CHO [18] and C_2H_5CHO.[12] The observation of the EPR signals due to the peroxy-radicals at low degrees of conversion of acetaldehyde and propionaldehyde (~10%) and the high selectivity of the reaction with respect to peroxyacids (~90%)[67] as well as the parallel course of the peroxy-radical and RCO_3H accumulation curves[18] served to identify the $RC\dot{O}_3$ radicals. An appreciable contribution to the EPR spectrum by radicals of the type $R\dot{O}_2$ was ruled out by the observation that the kinetics of the accumulation of their radicals were inconsistent with the kinetics of the accumulation of ethyl hydroperoxide.[26] Under the experimental conditions, the radicals accumulated in accordance with the rate law characteristic of an intermediate, while the yield of the hydroperoxide increased continuously.

The presence of $H\dot{O}_2$ radicals in the high-temperature oxidation of formaldehyde was indicated by the detection of hydrogen peroxide in the reaction products[57,61,68-71] and by the direct recording of the EPR spectra of the $H\dot{O}_2$ radical.[72]

The identification was based on a comparison of the spectra with the EPR spectra of the $HO_2^{\cdot}$ radicals quoted in the literature[73-76] and on the basis of the parallel behaviour of the radical and H_2O_2 accumulation curves.

The question of the nature of the chain propagating species under the conditions of the low-temperature oxidation of formaldehyde has been discussed[4] as a function of the actual pathway of the reaction of the HĊO radical with O_2 leading to the formation of HO_2 or $HCO_3^{\cdot}$ radicals.

$$\dot{HCO} + O_2 \begin{cases} \longrightarrow HO_2^{\cdot} + CO; & (1a) \\ \longrightarrow HCO_3^{\cdot}; & (1b) \\ \longrightarrow \cdot OH + CO_2. & (1c) \end{cases}$$

The results of studies in recent years of the reactions of the HĊO radicals with oxygen by infrared spectroscopy,[77] mass spectrometry,[78] and intracavity laser spectroscopy (ICLS) combined with flash photolysis,[79] as well as the direct detection of the $HO_2^{\cdot}$ radicals by EPR[80] indicate the preferential formation of $HO_2^{\cdot}$ radicals. The source of the HĊO radicals was either the reaction of formaldehyde with H atoms obtained by a high-frequency discharge in hydrogen or the photolysis of CH_2O.[81]

On the assumption that reaction (1a) takes place, its rate constant has been determined[78] by following directly the concentration of the HĊO radicals and on the basis of data concerning the competition of the reactions of the HĊO radicals with O_2 and O. In another study[77] a band corresponding solely to the $HO_2^{\cdot}$ radical was observed in the infrared spectrum of the products of the reaction of the HĊO radicals with oxygen at room temperature and no bands were found which could be attributed to the $HCO_3^{\cdot}$ radical. The study of the kinetics of the destruction of the HĊO radicals in the photolysis of CH_2O and CH_3CHO in the presence of O_2 by the ICLS method[79] made it possible to determine the rate constants for the overall reaction (1). On the basis of the lack of a dependence of k_1 on pressure in the range 0.2–76 kPa, it was concluded that either the $HO_2^{\cdot}$ radicals are formed preferentially or that the $HCO_3^{\cdot}$ radicals formed decompose rapidly into $CO(CO_2)$ and $HO_2^{\cdot}(\dot{O}H)$. Calculations by the LCAO method have shown[82] that an excited $HCO_3^{\cdot}$ radical is formed in reaction (1b) and can rapidly decompose into ȮH and CO_2. In view of the fact that the yield of CO_2 in the photolysis of CH_2O is low, it has been suggested that at room temperature reaction (1a) competes successfully with the stage (1b) indicated above.

The study of Osif and Heicklen[83] showed that $k_{1b}/k_{1a} = 5 \pm 1$ in the determination of the rates of reactions (1a) and (1b) from the known concentrations of CO, CO_2 and HCO_2H. However, other pathways leading to the formation of HCO_2H,[84] which differ from the reaction sequence $HCO_3^{\cdot} \rightarrow HCO_3H \rightarrow HCO_2H$ and associated, in particular, with secondary processes occurring in the system owing to the presence of CH_2O and H_2O_2 were not ruled out.[61]

The kinetics of the photolysis of CH_2O in a mixture containing O_2 and in the presence of CO_2 have been investigated at 298 K.[84] The quantum yields of H_2, CO, and CO_2 and the consumption of O_2 were determined. Since $\Phi_{H_2} \gg 1$ and $\Phi_{CO} \gg 1$ (Φ is the quantum yield), the authors proposed a reaction mechanism on the basis of which the following expression was obtained for the ratio of the rate constants (M is any kind of species):

$$\frac{k_{1b}[M]}{k_{1b}[M] + k_{1a}} \geqslant 0.049 \pm 0.017.$$

The question of the nature of the chain propagating active centre in the low-temperature oxidation of CH_2O was finally resolved after the direct detection of the $HO_2^{\cdot}$ radicals.[17]

Convincing evidence that peroxy-radicals are the chain propagating active centres was obtained by analysing the kinetics of the thermal oxidation of aldehydes and the following of its features: (1) the attainment of the maximum concentration of the $RCO_3^{\cdot}$ or $HO_2^{\cdot}$ radicals (depending on the object of study) simultaneously with the attainment of the maximum rate of consumption of the aldehyde; (2) the quantitative correspondence between the change in the rates of consumption of the aldehyde and the concentrations of the corresponding peroxy-radicals as the experimental conditions are varies.[12,17,18,26,67,72]

Information concerning the elementary rate-limiting reaction

$$RCO_3^{\cdot} + RCHO \rightarrow RCO_3H + R\dot{C}O$$

obtained indirectly by analysing the molecular products, has been published[31,85] and is presented in Table 1. The rate constants for this reaction have been determined[67] by measuring the concentration of the $RCO_3^{\cdot}$ radicals by EPR and the rate of accumulation of the peroxyacid in the gas-phase oxidation of CH_3CHO or C_2H_5CHO at low degrees of conversion. The rate constants are listed in Table 1.

Data concerning the elementary step

$$HO_2^{\cdot} + CH_2O \rightarrow H_2O_2 + \dot{HCO}$$

have been obtained[86,87] and are also presented in Table 1.

Table 1. The rate constants for the reactions of peroxy-radicals with aldehydes.

Reaction	A, cm^3 molecule^{-1} s^{-1}	E_a, kJ mol^{-1}	k, cm^3 molecule^{-1} s^{-1}	T, K	Remarks	Refs.
$HO_2^{\cdot} + CH_2O \rightarrow H_2O_2 + \dot{HCO}$	$1.6 \cdot 10^{-12}$ $1.6 \cdot 10^{-11}$ $1.9 \cdot 10^{-11}$	44.7 59.3 43.5±12.5	$1.6 \cdot 10^{-15}$ —	773	Slow $H_2 + O_2 + N_2 + CH_2O$ oxidation reaction CH_2O oxidation reaction, EPR method	[86] [87]
$CH_3CO_3^{\cdot} + CH_3CHO \rightarrow$ $\rightarrow CH_3CO_3H + CH_3\dot{C}O$	— — $(5.7 \pm 2.2) \cdot 10^{-12}$	30±4 28.4±4.18 33.4±3.2	$(1.3 \pm 0.3) \cdot 10^{-17}$ — —	293 360–403 415–473	Photochemical CH_3CHO oxidation reaction, analysis of molecular products CH_3CHO oxidation reaction initiated by $(CH_3)_3COOH$ Thermal CH_3CHO oxidation reaction, EPR method	[31] [85] [67]
$C_2H_5CO_3^{\cdot} + C_2H_5CHO \rightarrow$ $\rightarrow C_2H_5CO_3H + C_2H_5\dot{C}O$	— $(7.0 \pm 1.3) \cdot 10^{-12}$	28±2 32.2±2.1	$(7.2 \pm 0.2) \cdot 10^{-17}$ —	295 438–488	Photochemical C_2H_5CHO oxidation reaction, analysis of molecular products Thermal C_2H_5CHO oxidation reaction, EPR method	[31] [67]

Notation: A is the pre-exponential factor, E_a the activation energy, k the rate constant, and T the temperature.

On the basis of data showing a decrease of the induction period and the slow hydrogen oxidation reaction in the presence of added formaldehyde, the reaction mechanism, involving the reactions of the active species with CH_2O has been analysed with the aid of a computer, which made it possible to estimate the rate constant at 773 K.[86] The rate constant for this reaction has been measured by EPR.[87] The approach was similar to that used by Paronikyan et al;[67] the source of the $HO_2^{\cdot}$ radicals was the CH_2O oxidation reaction.

III. THE ROLE OF HETEROGENEOUS FACTORS IN THE OXIDATION OF ALDEHYDES

In the early studies of the oxidation of formaldehyde, few data were published concerning the influence of heterogeneous factors.[36,88,89] A decrease of the reaction rate[36] or a change in the composition of the products with increase of the S/V ratio was noted. In particular, a sharp increase in the yield of CO_2 compared with CO has been observed.[88]

Experiments in a reactor which had been treated with boric acid, inert with respect to decomposition of peroxy-compounds, leads to an appreciable increase in their yield.[59,90]

The observed discrepancies between results obtained by different workers (for example, the presence of an induction period and peroxides[59,89-91] or their absence[92]) has been attributed[60] to differences between the rates of the heterogeneous decomposition of the peroxy-compound, namely HCO_3H, in different experiments. Despite the lack of clear-cut evidence for the formation of HCO_3H, the above study[60] is valuable because the influence of the nature of the surface on the character of the kinetics of the oxidation of formaldehyde was noted in it for the first time.

Studies[93,94] whose authors noted that the treatment of the reactor surface with KCl leads to the inhibition of the homogeneous reaction and did not assume that both the formation and destruction of the active species proceed heterogeneously merit attention.

The influence of the surface of the reaction vessel on the CH_2O oxidation reaction was studied in greater detail by Markevich and Filippova.[68] in clean reactors the reaction proceeds with formation of a considerable amount of hydrogen peroxide (~27% of the initial aldehyde), while in reactors treated with various substances (KCl, CsCl, and $K_2B_4O_7$) the peroxide is not observed and the reaction proceeds at an almost constant rate. A similar dependence of the yield of H_2O_2 on the nature of the surface has been observed in other investigations.[71,72,95,96] The different data obtained have been accounted for in terms of different rate constants for the heterogeneous destruction of hydrogen peroxide and $HO_2^{\cdot}$ radicals on different surfaces.

Thus the variable data definitely indicate the dependence of the yield of H_2O_2 on the nature of the surface. As regards radicals, the first experimental proof of their formation has been obtained by Vardanyan and co-workers.[72,87] In the high-temperature oxidation of CH_2O in an untreated reactor and a reactor treated with boric acid, the $HO_2^{\cdot}$ radicals,[72] whose concentration reached 0.1% of the initial aldehyde, were detected together with considerable amounts of hydrogen peroxide. In reactors treated with salts, hydrogen peroxide and the $HO_2^{\cdot}$ radicals were not detected. Direct experiments have shown[87] that the rate of the heterogeneous destruction of the $HO_2^{\cdot}$ radicals in an untreated reactor and in a reactor treated with boric acid is low but increases appreciably on passing to reactors treated with salts.

In terms of their influence on the rate of the formaldehyde oxidation reaction and the composition of its products, the surfaces investigated have been divided into two groups.[97] A similar subdivision has also been carried out in another study.[98] In the reactors of the first group (reactors pretreated by the reaction taking place or treated with boric acid) the rate of reaction is high and the oxidation proceeds via a degenerate branched chain mechanism and the agent responsible for the chain branching is hydrogen peroxide. The effective activation energies, determined from the maximum rate of consumption of formaldehyde, are 109–125 kJ mol^{-1}. In the reactors of the second group (reactors treated with a salt) the rate of reaction is almost constant and is appreciably lower; no hydrogen peroxide has been detected in the products. The influence of the surface is reflected in a sharp increase of the effective activation energies (209 kJ mol^{-1}) compared with the reactors of the first group. Similar characteristics of the dependence on the nature of the surface have been observed also in the low-temperature oxidation of formaldehyde in reactors treated with boric acid and CsCl.[17]

On the basis of experimental studies and the analysis of the available literature data, the following mechanism has been proposed[56,97] for the oxidation of CH_2O:

$$CH_2O + O_2 \rightarrow H\dot{C}O + HO_2^{\cdot},$$
$$H\dot{C}O + O_2 \rightarrow HO_2^{\cdot} + CO,$$
$$HO_2^{\cdot} + CH_2O \rightarrow H_2O_2 + H\dot{C}O,$$
$$H_2O_2 + M \rightarrow 2OH + M,$$
$$\dot{O}H + CH_2O \rightarrow H_2O + H\dot{C}O,$$
$$\dot{O}H + H_2O_2 \rightarrow H_2O + HO_2^{\cdot},$$
$$H_2O_2 \xrightarrow{\text{wall}} \text{destruction},$$
$$HO_2^{\cdot} \xrightarrow{\text{wall}} \text{destruction},$$
$$HO_2^{\cdot} + HO_2^{\cdot} \rightarrow H_2O_2 + O_2.$$

Extremely convincing evidence for the alteration of the rate of the heterogeneous destruction of peroxy-radicals on passing from reactors of the first group to those of the second has been obtained by EPR.[87,99-101] The heterogeneous decomposition of hydrogen peroxide follows from the comparative analysis of data obtained in a study of the gas-phase decomposition of hydrogen peroxide as a function of the nature of the surface in glass reactors, both thoroughly cleaned[102] and treated with boric,[103,104] phosphoric,[105] and hydrofluoric acids[106] in the temperature range 573–873 K. It has been noted that at approximately 693–698 K a transition from a heterogeneous to a homogeneous reaction is observed. The homogeneous reaction mechanism is indicated, in particular, by the sharp increase of the effective activation energy—from 42 to 230 kJ mol^{-1}.[105] An increase of the reactor diameter leads to a decrease in the rate of decomposition of radicals.[104] In a reactor treated with boric acid,[103,104] the decomposition of H_2O_2 is difficult, and, according to the authors of one of the investigations,[102] a thoroughly clean glass surface is more effective for the conservation of H_2O_2.

The need to include the homogeneous recombination of the $HO_2^{\cdot}$ radicals arises from the experimentally observed dependence of the maximum $HO_2^{\cdot}$ radical concentration on the concentration of the initial aldehyde; this dependence is described by a curve which tends to a limit.[72]

The validity of the proposed mechanism and the characteristic features of the dependence of the reaction kinetics on the nature of the surface which follow from it have been confirmed with the aid of a mathematical model.[107]

There is very little information about the influence of the nature and state of the surface of the reaction vessel on the kinetics of the oxidation of acetaldehyde and propionaldehyde

under static conditions. According to published data, the effective activation energies for the oxidation of CH_3CHO and C_2H_5CHO are much lower (37.6–83.6 kJ mol^{-1}) than for the oxidation of CH_2O, where the effective activation energy is 117–209 kJ mol^{-1}.[5,8]

Pease's study[108] merits special attention because of the novelty of the conclusions reached on the basis of extremely limited information concerning the influence of the nature of the surface on the composition of the products and the rate of the low-temperature oxidation of acetaldehyde. He showed that the rate of reaction is 4–5 times higher in a reactor treated with KCl than in one washed with nitric acid. The maximum yield of CH_3CO_3H was observed in a reactor washed with nitric acid, while the highest yield of CO_2 was noted in a reactor treated with KCl. The amount of CO_2 formed in packed reactors was appreciably higher. By analogy with formaldehyde[96] and H_2,[108] a sharp decrease in the rate of reaction was to be expected in the reactor treated with KCl, since it is known that in this case the rate of destruction of active centres is higher.[87,98]

On the basis of these experimental results, Pease[108] suggested that, in the gas-phase oxidation of CH_3CHO, the chains are initiated on the surface as a consequence of the decomposition of CH_3CO_3H or the $CH_3CO_3^{\cdot}$ radical. Later, the observed dependence of pressure pulsations on the nature of the surface of the reaction vessel in the oxidation of acetaldehyde was also attributed[41] to the heterogeneous decomposition of RCO_3H but this time via a molecular mechanism. According to the authors,[41] the heat evolved in this process initiates a cold flame. However, it has been shown recently that the initiation of the flame is more likely to be the cause rather than the consequence of thermal heating.[110]

Studies[111,112] of the influence of the nature of the surface of a reactor treated with metal halides on the oxidation of acetaldehyde have led to the conclusion that the surfaces catalysing the decomposition of RCO_2H also catalyse the oxidation of CH_3CHO.

A relation has been established in a number of studies[32,108,113] between S/V and the rate of oxidation of CH_3CHO. The proposed explanations are contradictory. Heterogeneous initiation and chain termination have been suggested by Pease,[108] while McDowell and Thomas[32] postulated only a homogeneous process as did their earlier investigation[114] and the study of Combe et al.[39]

Since the calculated activation energies proved to depend on S/V, it was suggested that the corresponding stage is heterogeneous. If the initiation had been homogeneous, one might expect an activation energy of 171.4 kJ mol^{-1},[115] while the value actually obtained[116] is 121.2 kJ mol^{-1}. The possibility of the heterogeneous chain initiation in the oxidation of acetaldehyde has been demonstrated by EPR.[117] The available data show that at low temperatures heterogeneous initiation can predominate over homogeneous initiation.

Data on the influence of the nature and cleanliness of the reactor surface on the rate of the process and its activation energy, obtained in two investigations,[24,44] also merit attention. A marked dependence of the rate of reaction and of the ratio of the yields of the products of the low-temperature oxidation of acetaldehyde (peroxyacetic and acetic acids) on the specific concentration of the substance deposited on the reactor surface has been established recently.[112] The maximum yield of CH_3CO_3H was observed in the reactor treated with a 0.1% KCl solution, while the yield of CH_3CO_2H changed only slightly.

Using the above set of reactions (see Section II) for the description of the acetaldehyde oxidation process, Dixon et al.[22] obtained activation energies ranging from 0 to 66.9 kJ mol^{-1} in the temperature range 318–393 K, on the basis of which they concluded that the branching process is heterogeneous. A similar hypothesis has been put forward by Hardacre et al.[44]

Inspection of the available experimental data obtained under static conditions establishes that a detailed analysis of the products has been carried out only for acetaldehyde. The complete absence of detailed kinetic results concerning the oxidation of propionaldehyde is noteworthy. The sensitivity of the reaction to the nature and state of the surface of the reaction vessel observed in a number of investigations has not been reflected in the proposed mechanisms, which in essence describe a homogeneous process. The conclusion concerning the proposed elementary stages has been reached only on the basis of the analysis of the molecular products. There are no clearly well-founded data concerning the nature of the chain branching stage. The mechanisms of the gas-phase oxidation of CH_3CHO and C_2H_5CHO have been constructed formally by analogy with the liquid-phase oxidation,[46,118,119] which has been studied in greater detail.

Table 2. Characteristics of the aldehyde oxidation reactions.

Compound	c_0, %	T, K	10^{-16} w_{max}, cm^{-3} s^{-1}	Radical	10^{-13} c_r, cm^{-3}	Peroxide	10^{-16} c_p, cm^{-3}	Refs.
Reactors of first group								
CH_2O	1	850	42	$HO_2^{\cdot}$	12	H_2O_2	1	[71, 107]
CH_2O	5	718	1.8	$HO_2^{\cdot}$	2	H_2O_2	1	[17]
CH_3CHO	20	448	2	$CH_3CO_3^{\cdot}$	2.5	CH_3CO_3H	56	[11, 21]
CH_3CHO	2.5	498	0.3	$CH_3CO_3^{\cdot}$	5.6	CH_3CO_3H	6–6.2	[10, 19]
CH_3CHO	1.5	598	8	$CH_3CO_3^{\cdot}$	—	CH_3CO_3H	2	[19, 21]
CH_3CHO	1.5	623	10	$CH_3CO_3^{\cdot}$	10	CH_3CO_3H	0.72	[19, 21]
C_2H_5CHO	8	448	0.35	$C_2H_5CO_3^{\cdot}$	~1	$C_2H_5CO_3H$	8	[12]
C_2H_5CHO	2.1	564	0.3	$C_2H_5CO_3^{\cdot}$	1	$C_2H_5CO_3H$	1.3	[26]
Reactors of second group								
CH_2O	1	900	12	—	—	—	—	[71, 107]
CH_2O	5	723	0.2–0.25	—	—	—	—	[17]
CH_3CHO	20	448	10	$CH_3CO_3^{\cdot}$	11	CH_3CO_3H	1.9	[11, 21]
CH_3CHO	2.5	498	0.28	$CH_3CO_3^{\cdot}$	3.6	CH_3CO_3H	0.3	[10, 19]
CH_3CHO	1.5	598	3.2	$CH_3CO_3^{\cdot}$	—	CH_3CO_3H	<0.1	[19, 21]
CH_3CHO	1.5	623	4	$CH_3CO_3^{\cdot}$	2.5	CH_3CO_3H	<0.1	[19, 21]
C_2H_5CHO	8	448	0.5	$C_2H_5CO_3^{\cdot}$	1.3	$C_2H_5CO_3H$	3.8	[12]
C_2H_5CHO	2.1	564	0.26	$C_2H_5CO_3^{\cdot}$	0.5	$C_2H_5CO_3H$	—	[26]

Notation: c_0 is the initial concentration of the aldehyde in air at atmospheric pressure, w_{max} the maximum reaction rate, c_r the maximum concentration of radicals, and c_p the maximum concentration of the peroxide.

The first detailed investigation of the kinetics of the oxidation of CH_3CHO and C_2H_5CHO as a function of the nature of the surface has been carried out by Oganesyan and coworkers[18–21] and by Oganesyan[26] respectively. At 448 K the rate of oxidation of CH_3CHO in a reactor of the second group is ~4–5 times higher than in a reactor of the first group; a 40% conversion of acetaldehyde in a reactor of the second group was observed for t = 25 s (t is the residence time of the reaction mixture in the reactor) and for t = 90 s in a

reactor of the first group. The maximum yields of the peroxyacids also differ. The yield in a reactor treated with a salt amounts to 5–7% relative to the initial aldehyde, while in a reactor conditioned by the reaction itself it is 18–20%. An increase of temperature to 499 K results in an interesting phenomenon: the rates of the process in reactors of both types are similar. Up to 25% conversion of acetaldehyde, its consumption in the two cases is described virtually by the same S-shaped curve. The yield of CH_3CO_3H is appreciable in reactors of the first group (17–18%) and low in those of the second group (a fraction of one per cent). Considerable amounts of CH_3CO_3H have been observed[19] in the temperature range 598–648 K in a reactor treated with boric acid, the amount diminishing with increase of temperature: the maximum yields of CH_3CO_3H are 10–11% at 598 K and only 2% of the initial aldehyde at 648 K. In a reactor treated with a salt the amount of CH_3CO_3H is apparently below the sensitivity of the analysis.

The fact that the reaction proceeds autocatalytically in reactors of both types merits attention. However, in contrast to the low-temperature range, the rate of consumption of the aldehyde in a reactor of the first group is ~3–4 times greater (at 623 K) than in a reactor of the second group. The concentrations of the peroxy-radicals are correspondingly greater in a reactor treated with boric acid; Table 2 presents certain characteristic data.

The decreased yield of the organic peroxide with increase of temperature is explained by the increased rate of decomposition of both RCO_3H and the CH_3CO and $CH_3CO_3^{\cdot}$ radicals. It has been established by EPR[10] that the rate of decomposition of the peroxide on a surface treated with a salt is much higher than on one treated with boric acid. In contrast to the low-temperature range, in a reactor treated with boric acid hydrogen peroxide is detected in the CH_3CHO oxidation products, the shape of its accumulation curve differing from that for RCO_3H. Measurable amounts of H_2O_2 are detected at a later stage in the reaction than is RCO_3H. For example, at 623 K and for $t = 0.3$ s the CH_3CO_3H concentration is 2%, while that of hydrogen peroxide is only 0.1%.

Studies of the kinetics of the low-temperature oxidation of propionaldehyde[12] showed that the kinetic behaviour of the system in reactors of both groups is similar to that observed for acetaldehyde. As before, the reaction takes place with autoacceleration, the rate of consumption of the aldehyde and the maximum concentration of the $RCO_3^{\cdot}$ radicals being higher in reactors of the second group. The yields of peroxypropionic acid also differ appreciably: at 423 K and for $t = 2$ min its yield is 1.7% in a reactor treated with KCl and 4.7% of the initial aldehyde in one treated with boric acid.

It has been established[12] that, although the yield of $C_2H_5.CO_3H$ in a reactor treated with KCl is lower, a new organic peroxide, namely ethyl hydroperoxide, as well as ethanol are detected in the reaction product; furthermore, ethylene, detected in a reactor treated with boric acid, is absent. It was concluded that, under conditions favourable for the decomposition of the peroxyacid, the $C_2H_5^{\cdot}$ radicals formed react with oxygen, giving rise to the $C_2H_5O_2^{\cdot}$ radicals, whose subsequent reaction with the aldehyde leads to the formation of ethyl hydroperoxide. The experimentally established influence of the nature of the surface on the yield of the products C_2H_4 and $C_2H_5O_2H$ led to the hypothesis that the reactions $C_2H_5^{\cdot} + O_2 \rightarrow C_2H_4 + HO_2^{\cdot}$ and $C_2H_5^{\cdot} + O_2 \rightarrow C_2H_5O_2^{\cdot}$ take place partly on the reactor surface under the experimental conditions.

With increase of the experimental temperature to 431–531 K, a change in the ratio of the rates of consumption of C_2H_5CHO and of the concentrations of the radicals is observed in reactors of both types, as in the case of acetaldehyde; the ratios are higher in a reactor of the first group (Table 2). It has been established that the yields of $C_2H_5CO_3H$ and $C_2H_5.O_2H$ depend on the nature of the surface of the reaction vessel. In the case of a surface which is effective for the decomposition of peroxides and radicals, the yield of the peroxyacid is lower and that of the hydroperoxide is higher. This has been explained by the fact that the formation of the hydroperoxide is due to the reactions of the $C_2H_5^{\cdot}$ radicals arising in the course of the decomposition of the C_2H_5CO radicals and the peroxyacid.

Analysis of experimental data (Table 2) has shown that, whereas from the standpoint of the involvement of the peroxy-compound in the chain-branching stage the oxidation reactions of formaldehyde, acetaldehyde, and propionaldehyde are similar, in terms of the influence of the nature of the reactor surface they are different. The oxidation of CH_3CHO and C_2H_5CHO proceeds with autoacceleration in reactors of all types. The main intermediate, responsible for the branching, is the corresponding peroxyacid RCO_3H, while the chain propagating active centres are the $RCO_3^{\cdot}$ radicals. The fact that in the low-temperature range the rate of reaction and the concentration of the chain propagating species are low in reactors treated with salts, which are effective inhibitors[3] of the epoxidation processes, despite the intense destruction of the radicals merits attention.

It has been shown for formaldehyde that the rate of reaction in reactors treated with salt is greatly reduced, while the concentration of the active centres becomes lower than the sensitivity of the analysis. The opposite behaviour has been observed for acetaldehyde and propionaldehyde. This is due to the fundamental difference between the natures of the chain branching stages in the oxidation of formaldehyde, on the one hand, and acetaldehyde and propionaldehyde, on the other. This is also indicated by the appreciable difference between the effective activation energies for the processes and the compositions of the reaction products as a function of the nature of the surface. Whereas in the case of CH_2O the activation energy varies from 108.7 kJ mol^{-1} for a surface treated with an acid to 209 kJ mol^{-1} for a surface treated with a salt, in the case of acetaldehyde and propionaldehyde, the activation energy is 37.6–83.6 kJ mol^{-1}, being smaller for a surface treated with a salt.

The kinetic manifestation of the influence of the nature of the surface on the formaldehyde oxidation reaction does not conflict with the idea that there is a stage involving the heterogeneous destruction of the $HO_2^{\cdot}$ radicals and H_2O_2—the product responsible for the branching. For two successive representatives of aliphatic aldehydes, this explanation is invalid. If the decomposition of the intermediate (the peroxyacid) were heterogeneous and involved the formation of molecular products only, the CH_3CHO and C_2H_5CHO oxidation reactions should have been retarded in reactors of the second group in the low-temperature range. Clearly, apart from the heterogeneous chain termination stage, a surface reaction which generates active centres in the gas phase must also occur. This reaction is the decomposition of the peroxyacid on the surface via a radical mechanism with liberation of some of the radicals into the gas phase.

The occurrence of the heterogeneous chain branching has been confirmed with adequate reliability by the autocatalytic character of the process observed regardless of the nature of the surface, the high rates of reaction, and the high concentrations of the active centres in a reactor whose surface (treated with a salt) is effective in the destruction of radicals.

The heterogeneous chain branching is also supported by the results of experiments involving adsorption on the cold surface of the reactor of small amounts of CH_3CO_3H, which leads to the auto-ignition of the acetaldehyde–oxygen mixture

on reheating as a consequence of the heterogeneous decomposition of CH_3CO_3H.[120,121] The temperature of the induced auto-ignition then depends both on the amount of the adsorbed CH_3CO_3H and on the S/V ratio; with increase of S/V, the auto-ignition temperature falls sharply.

According to the available data,[1-3] the increase of S/V leads as a rule to a decrease in the rate of the chain process, which indicates heterogeneous chain termination. However, the influence of the surface is not exhausted by this finding. In early investigations[122-131] the possibility of heterogeneous chain initiation and branching was assumed. The latter possibility was subjected to theoretical analysis in a number of investigations.[1,131-133] So far, there are few experimental data concerning heterogeneous branching. One may note studies[126-130] which dealt with the low-temperature oxidation of hydrocarbons: propane, ethane, and methane. The observed anomalous influence of the surface on the rate of the corresponding stage of the chain process, namely the increase of the rate with increase of S/V, was attributed to heterogeneous chain branching.

Yet another experimental piece of evidence for heterogeneous chain branching in the CH_3CHO and C_2H_5CHO oxidation reactions is provided by the discovery of the radical decomposition of the vapours of the organic peroxides CH_3CO_3H, HCO_3H, CH_3OOH, $C_2H_5CO_3H$, and $(CH_3)_3COOH$ on a solid surface with liberation of some of the radicals from the surface to the gas phase.[134-147] The experiments on the decomposition of the peroxy-compounds were performed mainly at atmospheric pressure in a stream of nitrogen containing small amounts of O_2 at temperatures from ambient up to 498 K. In a number of instances at low pressure the peroxyacid was supplied to the catalyst without dilution with an inert gas. The solid surfaces were those of the reactors of the first and second groups and also metallic platinum, gold, and silver. The residence time in the reactor was varied from several seconds to 10^{-3}–10^{-4} s. In the course of the experiments it was established that, in the absence of catalysts, the decomposition proceeds via a first-order reaction with respect to the peroxy-compound with formation of radicals, which are partly transferred to the gas phase. The detection of peroxy-radicals in the cold trap, placed in the EPR cavity, serves as experimental evidence for the radical decomposition. The heterogeneous character of the decomposition of the peroxy-compounds has also been confirmed by the low effective activation energies, not exceeding 54.3 kJ mol^{-1}.

The general character of the radical decomposition on many solid surfaces has been established in relation to peroxyacetic acid. The detection of the $CH_3CO_3^{\cdot}$ radicals[134] and analysis of the molecular products in the course of the decomposition on platinum[143] led to the conclusion that the peroxyacid dissociates with homolysis of the peroxide bond. This is supported by the finding that the amount of CO_2 formed reached 90% of the initial peroxide. The formation (in the course of the decomposition of organic peroxy-compounds) of OH_{ads} radicals adsorbed on the surface has been demonstrated as a result of the investigation of the methyl hydroperoxide decomposition reaction on a platinum wire in the presence of small amounts of added CO.[143] Under conditions ruling out homogeneous reactions, the formation of additional amounts of CO_2, attributed to the interaction of OH_{ads} with CO, has been observed.

It has been shown that, from the standpoint of the generation of radicals on the surface and their transfer into space, the activities of the catalysts decrease in the following sequence of metals:[141] Pt > Au > Ag, and in the following sequence of alkali metal chlorides:[144] LiCl > NaCl > KCl > RbCl > CsCl.

Comparison of the kinetics of the decomposition reactions of peroxyacetic acid on silver and potassium chloride led to the conclusion that the metallic catalyst is more effective, particularly as regards the generation of radicals and their transfer into the gas phase. Analysis[139] of the ratio of the concentrations of the molecular products of the decomposition of peroxypropionic acid (C_2H_4 and C_2H_4O) made it possible to exclude the transfer of the radicals R from the surface into space.

In a number of instances[134-139] the yield of radicals is appreciable, amounting to 10% of the amount of the decomposed peroxide. A recent study of the radical decomposition of t-butyl hydroperoxide showed that the yield of the $CH_3OO^{\cdot}$ radicals reaches 90% of the decomposed hydroperoxide.[147]

It has been suggested that the heterogeneous decomposition of organic peroxides be used as a source of peroxy-radicals and OH_{ads} radicals for the initiation of the low-temperature oxidation reactions of organic compounds in order to investigate radical reactions.[148]

On the basis of data for the decomposition of organic peroxides on a solid surface, the kinetic curves for the accumulation of the $RO_2^{\cdot}$ radicals, and the analysis of molecular products, the following fundamental elementary steps leading to the formation of radicals have been proposed:[14]

$$CH_3CO_3H_{ads} \rightarrow CH_3CO_{2\,ads}^{\cdot} + \dot{O}H_{ads},$$
$$CH_3CO_{2\,ads}^{\cdot} \rightarrow CH_{3\,ads}^{\cdot} + CO_2,$$
$$CH_{3\,ads}^{\cdot} + O_2 \rightarrow CH_3O_{2\,ads}^{\cdot}$$
$$CH_3O_{2\,ads}^{\cdot} \rightarrow \text{partial transfer of radicals into gas phase.}$$

An important result of the experimental study of the kinetics of the heterogeneous radical decomposition of a peroxy-compound (a peroxyacid) is that the rate of the decomposition reaction on the surface of glass treated with a salt (second group) exceeds that in a reactor treated with boric acid (first group). This result agrees with the observed higher rate of oxidation of acetaldehyde and propionaldehyde in reactors treated with a salt, supporting the view that the branching stage is heterogeneous.

The establishment of the fact that the chain branching is heterogeneous has a number of consequences necessitating a detailed specification of the mechanism presented above by introducing certain possible surface processes involving the radicals formed. The following reactions may be included among them:

$$OH_{ads} + RCHO \rightarrow RCO_{ads} + H_2O, \quad (2)$$

$$RCO_{2\,ads} + RCHO \rightarrow RCO_2H + RCO_{ads}, \quad (3)$$

$$RCO_{ads} \rightarrow R_{ads} + CO, \quad (4)$$

$$RCO_{2\,ads} \rightarrow R_{ads} + CO_2. \quad (5)$$

Information concerning the possibility of the occurrence of reactions (4) and (5) has been published in a communication,[26] where it is shown that the yields of CO, CO_2, as well as C_2H_4 and $C_2H_5O_2H$ depend on the nature of the surface and increase with increase of S/V. The possibility of the occurrence of reaction (2) follows from the possibility of the reaction $OH_{ads} + CO \rightarrow CO_2 + H^{\cdot}$.[143] Depending on the experimental conditions (on the nature of the surface and the values of S/V), the ratio of the contributions of the heterogeneous and homogeneous stages can vary.

Modern ideas about the mechanism of the oxidation of acetaldehyde and propionaldehyde and, in particular, about the pathway leading to the formation of the products can be

formulated mainly in the form of the following sequence of elementary stages without claiming that it is complete:[21,26]

$$RCHO + O_2 \rightarrow R\dot{C}O + HO_2^{\cdot}, \quad (6)$$

$$R\dot{C}O + O_2 \rightarrow RCO_3^{\cdot}, \quad (7)$$

$$RCO_3^{\cdot} + RCHO \rightarrow RCO_3H + R\dot{C}O, \quad (8)$$

$$RCO_3H \xrightarrow{\text{wall}} RCO_2^{\cdot} + \dot{O}H, \quad (9)$$

$$RCO_3H \rightarrow RCO_2^{\cdot} + OH, \quad (10)$$

$$RCO_2^{\cdot} + RCHO \rightarrow RCO_2H + R\dot{C}O, \quad (11)$$

$$\dot{O}H + RCHO \rightarrow H_2O + R\dot{C}O, \quad (12)$$

$$RCO_3^{\cdot} \xrightarrow{\text{wall}} \text{destruction}, \quad (13)$$

$$2RCO_2^{\cdot} \rightarrow \text{products}, \quad (14)$$

$$RCO_3^{\cdot} \rightarrow RO^{\cdot} + CO_2, \quad (15)$$

$$RO^{\cdot} + RCHO \rightarrow ROH + R\dot{C}O, \quad (16)$$

$$R\dot{C}O \rightarrow R^{\cdot} + CO, \quad (17)$$

$$RCO_2^{\cdot} \rightarrow R^{\cdot} + CO_2, \quad (18)$$

$$RO^{\cdot} + O_2 \leftrightarrow RCHO + HO_2^{\cdot}, \quad (19)$$

$$R^{\cdot} + O_2 \rightarrow RO_2^{\cdot}, \quad (20)$$

$$RO_2^{\cdot} + RCHO \rightarrow RO_2H + R\dot{C}O, \quad (21)$$

$$R^{\cdot} + O_2 \rightarrow \text{olefin} + HO_2^{\cdot}, \quad (22)$$

$$RO_2^{\cdot} \rightarrow \text{olefin} + HO_2, \quad (23)$$

$$HO_2^{\cdot} + RCHO \rightarrow H_2O_2 + R\dot{C}O, \quad (24)$$

$$HO_2^{\cdot} + \dot{C}H_2O \rightarrow H_2O_2 + H\dot{C}O, \quad (25)$$

$$H_2O_2 + M \rightarrow 2\dot{O}H + M. \quad (26)$$

As already mentioned above, it is assumed that reactions (6), (9), (11), (12), (17), (18), (22), and (23) proceed both on the surface and in the gas phase.

The possibility of the homogeneous recombination of the $RCO_3^{\cdot}$ radicals is justified by experiments[66] in which acetyl peroxide was detected in the RCHO oxidation products and also by the tendency of the maximum concentration of the $RCO_3^{\cdot}$ radicals to reach a plateau with increase in the initial concentration of acetaldehyde.[18] The need to include reactions (24)–(26) arises from the direct detection of the $HO_2^{\cdot}$ radicals and hydrogen peroxide in the high-temperature oxidation of acetaldehyde and propionaldehyde.[26] Direct proof of the occurrence of the heterogeneous chain propagation stages can be provided by the study of the corresponding process at low pressures and temperatures under conditions ruling out homogeneous reactions.

Thus, whereas the mechanism of the oxidation of CH_2O can be regarded as in the main established, that of the oxidation of aliphatic aldehydes of the type RCHO requires further refinement in view of the observation that heterogeneous chain branching takes place.

IV. THE NEGATIVE TEMPERATURE COEFFICIENT OF THE MAXIMUM RATE OF REACTION

Studies devoted to the phenomenon of the negative temperature coefficient (NTC) of the maximum rate of reaction have been surveyed mainly in monographs.[2–4] The principal conclusion which follows from these investigations is that the phenomenon of the NTC is due to the thermal instability of a "critical" intermediate; however, the nature of this species is still controversial. The explanation proposed in a study,[149] where the competition of the reactions of radicals of the type $RO_2^{\cdot}$, $RO^{\cdot}$, $CH_3CO_3^{\cdot}$, and CH_3CO and of the interaction of the radicals $RO_2^{\cdot}$ and $CH_3CO_3^{\cdot}$ with acetaldehyde and the hydrocarbon respectively, leading to the formation of peroxy-compounds, in particular the peroxyacid responsible for the chain branching, merits special attention. With increase of temperature, the rate of formation of the peroxyacid diminishes, causing a fall in the overall rate of the reaction. Other workers adhere to a similar point of view.[150–151] The phenomenon of the NTC has been explained[152] by the competition between the chain propagation and isomerisation reactions of the radicals $RO_2^{\cdot}$ or $RCO_3^{\cdot}$.

The application of the EPR method to the study of the oxidation of propane made it possible to discover the chain propagating species for the reaction,[153,154] and to conclude that the phenomenon of the NTC is due to a change in the chain propagating species and the intermediates responsible for chain branching.[153] $RO_2^{\cdot}$ radicals and ROOH have been detected in the low-temperature range, while $HO_2^{\cdot}$ radicals and H_2O_2 have been found in the high-temperature range.

The phenomenon of the NTC in the aldehyde oxidation reactions has been investigated.[15,16] In the case of acetaldehyde the authors explained it by the contribution of the reverse reaction involving the decomposition of the $CH_3O_2^{\cdot}$ radicals; in the case of propionaldehyde the authors merely stated the fact of its existence. The kinetics of the oxidation of propionaldehyde at atmospheric pressure under flow conditions and at temperatures corresponding to the fall, the minimum, and the increase to a maximum reaction rate, namely 623, 683, and 803 K respectively, have been investigated comparatively recently by EPR.[155] In all cases the EPR spectra of peroxy-radicals were recorded. At 623 K considerable amounts of ethyl hydroperoxide and small amounts of peroxypropionic acid, formed from the peroxy-compounds, were found.

Analysis of the kinetics of the accumulation of C_2H_5OOH and peroxy-radicals enabled the authors[155] to conclude that the main contribution to the EPR spectrum comes from radicals of the type of $C_2H_5CO_3^{\cdot}$. The maximum concentration of the latter is attained (within the limits of experimental error) simultaneously with the attainment of the maximum rate of consumption of the aldehyde. This experimental finding served as proof that the chain propagating active centres in this temperature range are precisely the $RCO_3^{\cdot}$ radicals. The discovery of large amounts of CO and $C_2H_5.O_2H$ and the fact that the ratio $[CO]/[CO_2] > 1$ permitted the conclusion that the $R\dot{C}O$ decomposition stage makes a significant contribution. The decrease in the rate of consumption of the aldehyde at 683 K is accompanied by a decrease in the concentration of the peroxy-radicals and peroxy-compounds. A sharp increase of the concentration ratio $[CO]/[CO_2]$, which becomes ~10, is noteworthy. Such a sharp change in the ratio of the product concentrations has been explained[155] by the decrease of the rates of formation of the $C_2H_5CO_3^{\cdot}$ radical and organic peroxy-compounds as a consequence of the increase of the rate of decomposition of the $\dot{C}_2H_5CO$ radical, leading to a fall of the rate of the C_2H_5CHO oxidation reaction. At 803 K the $HO_2^{\cdot}$ radicals and

H_2O_2 were detected as intermediates, the maximum concentrations of the radicals and the rate of decomposition of propionaldehyde being attained almost simultaneously.

Analysis of the experimental data led the authors[155] to the conclusion that the chain propagating active centres in the region of the NTC consist predominantly of the $C_2H_5CO_3^{\cdot}$ radicals, whose concentration increases sharply with increase of temperature owing to their thermal instability and the thermal instability of the $C_2H_5\dot{C}O$ radicals. This causes an appreciable decrease of the concentration of the peroxy-compounds $C_2H_5CO_3H$ and C_2H_5OOH, which leads to a decrease in the rate of the process. On further increase of temperature, the rate of reaction again begins to rise, since the contribution by the degenerate chain branching process, responsible for the bimolecular decomposition reactions of hydrogen peroxide, begins to increase anew.

The results obtained permitted the conclusion that the phenomenon of the NTC in the oxidation of propionaldehyde is caused by the competition between the $C_2H_5\dot{C}O$ radical decomposition and oxidation reactions. As a consequence of this, the reaction mechanism changes, namely the nature of the chain propagating active centres and the peroxy-compounds responsible for the degenerate branching changes. In the region of the NTC these are the peroxy-radicals and organic peroxides, while at high temperatures the corresponding species are the $HO_2^{\cdot}$ radicals and hydrogen peroxide.

On the basis of the available information about the possibility of the heterogeneous decomposition of the $C_2H_5\dot{C}O$ radical,[26] one may expect an appreciable influence of the nature of the surface on the phenomenon of the NTC.[156] Depending on the change in the rate of decomposition of $C_2H_5\dot{C}O$, there is a possibility of narrowing or expanding the region of the negative temperature coefficient of the maximum rate of reaction.

In view of the fundamental similarity of the mechanisms of the oxidation of propionaldehyde and acetaldehyde, the above conclusions can be extended also to the oxidation of acetaldehyde in the region of the NTC of the maximum rate of reaction. The absence of the phenomenon of the NTC in the oxidation of CH_2O may be associated precisely with the fact that neither the $HCO_3^{\cdot}$ radicals nor HCO_3H are formed and the oxidation proceeds with formation of the $HO_2^{\cdot}$ radicals and hydrogen peroxide, albeit an appreciably lower rate, which however increases continuously with temperature, as a consequence of which the causes of the change in mechanism do not apply.

The ideas developed and the experimental data described above can help also in the understanding of the NTC phenomenon in the oxidation of hydrocarbons, in the course of which aldehydes and the corresponding peroxyacids are produced. The possibility of the formation of the latter at comparatively high temperatures (from 598 to 723 K) follows from experiments[19] carried out under flow conditions at atmospheric pressure and for short residence times of the reaction mixture in the reactor, i.e. under conditions which make it possible to remove relatively unstable products fairly rapidly from the reaction zone and to accumulate them until they attain concentrations susceptible to measurement.

V. CONCLUSION

Analysis of the experimental data on the oxidation of aldehydes makes it possible to explain the greater ease of the oxidation of CH_3CHO and C_2H_5CHO compared with CH_2O. This is associated in the first place with the fundamental difference in the character of the branching stage from the standpoint of both the nature of the products responsible for the branching and the site at which this reaction is localised (surface or space).

In the CH_3CHO and C_2H_5CHO oxidation reactions chain branching is caused by the heterogeneous radical decomposition of the corresponding peroxyacid, while in the CH_2O oxidation reaction it is due to the homogeneous bimolecular decomposition of hydrogen peroxide. As regards the behaviour of these two peroxy-compounds under corresponding conditions, it is known that peroxyacids decompose at a much higher rate and with a lower activation energy[134] than hydrogen peroxide.[157] The possibility of the heterogeneous radical decomposition of hydrogen peroxide has been demonstrated.[158–161] However, in the oxidation of formaldehyde at atmospheric pressure the rate of the heterogeneous radical decomposition of hydrogen peroxide is lower than the rate of its homogeneous bimolecular decomposition.

One cause of the low rates of oxidation of formaldehyde is the fact that the reaction chains are short,[2] in contrast to CH_3CHO and C_2H_5CHO, and that the chain propagating species in the reaction is the $HO_2^{\cdot}$ radical, whose interaction with the aldehyde proceeds with an activation energy of 46 kJ mol^{-1},[87] which is appreciably higher than the activation energies for the interaction of the $RCO_3^{\cdot}$ radicals with $CH_3.\dot{C}HO$ and C_2H_5CHO, amounting to 33.4 and 32.2 kJ mol^{-1} respectively.[67]

The formation of the peroxyacid in the oxidation of acetaldehyde and propionaldehyde and its absence in the oxidation of formaldehyde are caused by the different reactivities of the $H\dot{C}O$ and $R\dot{C}O$ radicals towards oxygen. The former reaction leads mainly to the formation of the $HO_2^{\cdot}$ radicals and the latter to the formation of the $RCO_3^{\cdot}$ radicals. Ultimately this is the reason why the formaldehyde oxidation reaction is somewhat isolated in the series of aliphatic aldehydes.

The experimental evidence for heterogeneous chain branching is important not only for the determination of the mechanism of the thermal oxidation of acetaldehyde and propionaldehyde but also for the further development of the theory of degenerate branched chain reactions, indicating the existence of a similar heterogeneous stage in many reactions exhibiting an "anomalous" sensitivity to the nature and state of the surface of the reaction vessel.

The survey of the experimental data permits the conclusion that the heterogeneous branching of homogeneous chains in the oxidation reactions of organic compounds proceeds more effectively at low temperatures and in the presence of long chains. From this standpoint, it is desirable to revise the existing schemes for the gas-phase oxidation of organic substances and to introduce, as far as possible, corrections to their mechanism, since in practice a corresponding reaction was not taken into account in constructing the mechanism, although the influence of the surface on these processes has not been denied in the literature.

The detection of peroxy-compounds in the high-temperature oxidation of aldehydes also indicates their involvement in chain branching in the oxidation reactions of hydrocarbons.

The results of studies[10,11,18–21,26] have led to a series of important practical conclusions, providing explanations of certain fundamental phenomena, which had been incomprehensible until recently. The observed[108] acceleration of the acetaldehyde oxidation reaction in reactors treated with KCl, as well as the influence of S/V and of the specific concentration of the KCl (deposited on the surface) on the rate and direction of the CH_3CHO oxidation reaction, the spontaneous inflammation of $CH_3CHO + O_2$ mixtures which have partly reacted at a lower temperature after their "quenching", and the spontaneous inflammation of artificial mixtures with added

peroxy-acetic acid[5] are explained by the degenerate chain branching. The observed pressure pulsations in the reactor treated with KCl at a lower temperature in the cold-flame oxidation of acetaldehyde are also caused by the radical decomposition of peroxyacetic acid, specifically by the increase of its rate on a given surface.

Thus the results of the study of the gas-phase oxidation of aldehydes obtained in recent years have significantly altered the existing ideas about the mechanisms of these processes. This has promoted the development of theoretical bases for technological processes for the preparation of valuable oxygen-containing compounds by treating the surface of the reactor or by altering the S/V ratio. In particular, ways have been found for increasing the selectivity in the oxidation of propionaldehyde to propionic[162] and peroxypropionic[12] acids and of acetaldehyde to peroxyacetic acid.[163]

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The Reactions of Acetals with Ozone

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Data concerning the composition of the products of the ozonisation of acetals, the stoichiometry of the process, and the influence of substituents and the structure of acetals on their reactivity, the effect of the polarity of the medium, the activation parameters for the process, and the kinetic isotope effects are surveyed and analysed. At lowered temperatures the process proceeds via a heterolytic mechanism, while with increase of temperature the fraction of ozone consumed due to the formation of free radicals rises.
The bibliography includes 60 references.

CONTENTS

I. Introduction 544
II. The products of the ozonolysis of acetals and related compounds 544
III. The contribution of radical reactions in the ozonolysis of acetals 547
IV. The influence of the structure of acetals and the conditions in their reactions with ozone on the rate of the process 548
V. The mechanism of the interaction of ozone with acetals 550

I. INTRODUCTION

The reactions of organic compounds with ozone, leading to various polyfunctional oxygen-containing compounds, are of considerable theoretical and practical interest.[1-3] However, the available information about the reactions of saturated hetero-organic compounds with ozone has not so far been surveyed or described systematically. It is known that, in the course of the ozonolysis of saturated oxygen compounds, substances containing carboxy-, carbonyl, and hydroxy-groups are formed.[4-9] The ozonolysis of acetals with linear and cyclic structures proceeds smoothly under mild conditions and with a high selectivity.[10-19] Since acetals can be readily obtained from cheap easily available petrochemical products, their use as the starting materials in organic synthesis is extremely promising. The ozonolysis of 1,1-dialkoxyalkanes and 1,3-dioxacyclanes leads to the formation of esters, alcohols, and glycol monoethers, ozone attacking only the methylene (or methylidyne) group adjoining two heteroatoms.[12,18] The principal publications devoted to this process are summarised and analysed in this review.

II. THE PRODUCTS OF THE OZONOLYSIS OF ACETALS AND RELATED COMPOUNDS

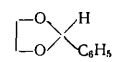
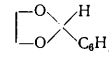
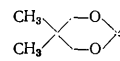
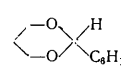
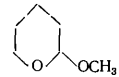
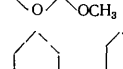
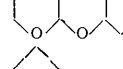
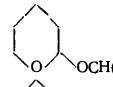
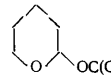
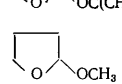
The first communication[11] stating that the reaction of ozones with acetals is rigorously specific, giving rise to quantitative yields of the corresponding esters of alcohols or glycol monoesters, was published in 1971. In later studies by the same workers,[12-16,20-23] a relation was established between the conformation of the acetal group and its reactivity towards ozone. It was shown that the reaction considered is general for acetals having linear and cyclic structures (Table 1).

The nature of the alkyl substituents in acyclic acetals does not influence the composition of the reaction products. However, significant differences are observed between the rates of oxidation; cyclic acetals react much faster than acyclic acetals (Table 1). Thus the complete oxidation of 1,3-dioxolans (I) and (II) required only 10 min, whereas exhaustive ozonolysis of the dimethoxyacetals (VI) and (VII) takes place in 13–15 h. Under these conditions, one mole of ozone reacts with one mole of the acetal, giving rise to one mole of the ester and one mole of oxygen.

The interaction of ozone with linear-cyclic acetals has been studied in relation to tetrahydropyranyl and tetrahydrofuryl ethers.[12,13]

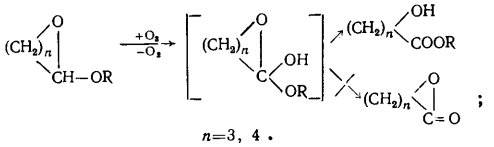
Treatment of 2-alkoxyoxacyclanes with ozone (Table 1) results in the exclusivie formation of esters of ω-hydroxy-acids; lactones and other products were not detected in the reaction mixture.[12,13]

Table 1. Ozonolysis of acetals at −18 °C in ethyl acetate.[11]

No.	Acetal	Product	Reaction time, h	Yield, %
(I)		$C_6H_5COOCH_2CH_2OH$	10*	100
(II)		$C_6H_{13}COOCH_2CH_2OH$	10*	98
(III)		$C_6H_{13}COOCH_2\overset{\displaystyle CH_3}{\overset{\vert}{C}}H_2OH$	1	98
(IV)		$C_6H_{13}COOCH_2CH_2CH_2OH$	2	97
(V)	$C_6H_{13}CH(OC_2H_5)_2$	$C_6H_{13}COOC_2H_5$	8	97
(VI)	cyclo-$C_6H_{11}CH(OCH_3)_2$	cyclo-$C_6H_{11}COOCH_3$	13	98
(VII)	$C_6H_{13}CH(OCH_3)_2$	$C_6H_{13}COOCH_3$	15	91
(VIII)			2	99
(IX)			1	91
(X)			3	91
(XI)			2	95
(XII)			6	85
(XIII)			6	87

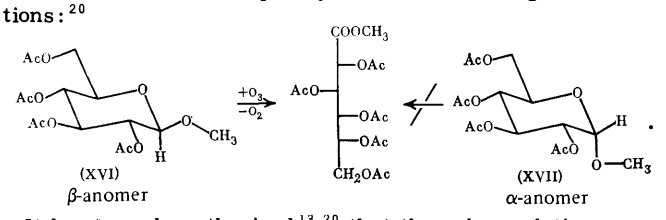
*The reaction time is given in minutes.

The formation of the products of this process is explained by the following scheme:[13]



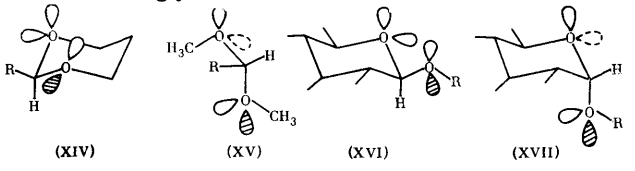
$n=3, 4$.

Subsequently the oxidation of a series of conformationally rigid α- and β-methylglucopyranosides was investigated.[12,20] The β-anomers were oxidised smoothly with ozone, while the α-anomers did not react. For example, methyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (XVI) is converted into methyl 2,3,4,5,6-penta-*O*-acetylgluconate, while the corresponding α-anomer (XVII) is completely inert under analogous conditions:[20]



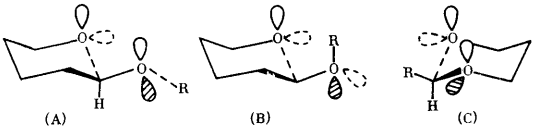
(XVI) β-anomer (XVII) α-anomer

It has been hypothesised[13,20] that there is a relation between the configuration of the acetal group and its reactivity with respect to ozone. For the successful occurrence of the reaction, there should be at each oxygen atom in the acetal an unshared electron pair such that its free orbital is oriented perpendicular to the plane including the C–H bond to be dissociated. This requirement is satisfied by acetals with a dioxan structure (XIV) and the most stable rotational isomers of the β-glycosides (XVI).



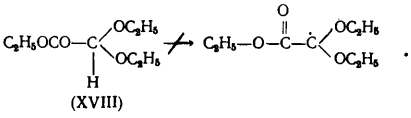
(XIV) (XV) (XVI) (XVII)

In the α-glycosides (XVII), the preferred conformation is that where the orbitals of the oxygen atoms in the ring are not oriented perpendicular to the plane containing the C–H bond and only the second oxygen atom has an orbital with the appropriate orientation; the oxidation with ozone does not therefore occur at an appreciate rate. For the preferred conformation of the linear acetal (XV),[13] the orientation of the oxygen orbitals is analogous to that in the α-glycosides (XVII). In order to interact with ozone, the dialkoxyalkane needs to assume another conformation, which ensures the required orientation of the orbitals (this is impossible for α-glycoside with their rigid chair conformation). However, the equilibrium concentration of any reactive conformer of a dialkoxyalkane is extremely insignificant, because the anomeric effect must be overcome for its formation and the rate of reaction, which depends on the concentration of this conformer, is extremely low. All the possible skewed conformers possible for the acetal group have been examined[20] and for each of them a rigid chemical model was selected and its reactivity with respect to ozone was determined. The experimental results obtained, summarised in a number of studies,[13,20,22,23] established that, of the six *gauche*-conformations possible for the acetal group, only three, namely (A), (B), and (C), are reactive with respect to ozone:



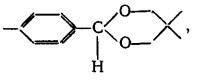
(A) (B) (C)

In these conformers the orbital of the unshared electron pair of each oxygen atom is oriented perpendicular to the plane containing the C–H bond. The results suggested[13] that a positive charge on the carbon atom of the acetal group should be generated in the transition state of the reaction. The appropriate disposition of the orbitals of the free electron pairs of each oxygen atom can readily stabilise such a positive charge. In the presence of the ethoxycarbonyl group this type of stabilisation is impossible and ethyl diethoxyacetate (XVIII) proved to be completely inert with respect to ozone. This rules out the possibility of a free-radical reaction mechanism because the presence of the ethoxycarbonyl group should facilitate the formation of the intermediate dialkoxyethoxycarbonylmethyl radical:



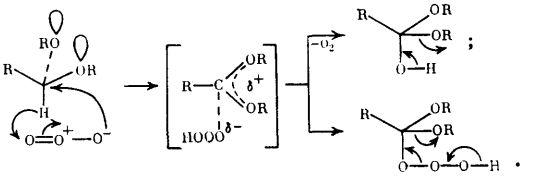
(XVIII)

The study of the reactivities of the acetals of *p*-substituted benzaldehydes



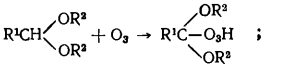
where R = OCH_3, H, or NO_2, showed that electron-donating groups accelerate the reaction, while electron-accepting groups retard it.

The set of the results obtained suggested the following process mechanism[13,20] [see also Section (V)]. Ozone reacts with the C–H acetal bond by a 1,3-insertion mechanism, forming either an α-hydroxyacetal and molecular oxygen or a hydrotrioxide:



These products decompose to an ester of an alcohol. It must be emphasised that ozone is inserted only for the conformation of the acetal group in which the orbital of the free electron pair of each oxygen atom has the antiperiplanar orientation in relation to the C–H bond.

In most investigations it has been suggested that the labile intermediates in the ozonolysis of unsaturated compounds are the corresponding hydrotrioxides.[13,20,24] The first spectroscopic evidence for the existence of hydrotrioxides was obtained in the study of the ozonolysis of ethers.[24] It has been observed recently[17,28] that the interaction of acetals with ozone results in the formation of hydrotrioxides, stable at −50 °C, which have been identified by ^{1}H NMR:



(XIX)—(XXII)

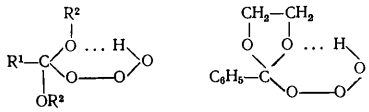
(XIX): $R^1=R^2=CH_3$

(XX): $R^1=CH_3$, $R^2=C_2H_5$

(XXI): $R^1=C_6H_5$, $R^2=CH_3$

(XXII): $R^1=C_6H_5$, $R^2R^2=(CH_2)_2$.

The ^{1}H NMR spectra contain two signals in the region of δ = 13 p.p.m. relative to Me_4Si. Since the position of the signals did not change appreciably on dilution, they were preferentially attributed to the proton of the OOOH group combined into six-membered rings by an intramolecular hydrogen bond:[28]



Although the origin of two signals of the proton in the O_3H group remains obscure, it is of interest to note that a similar observation has been made for the hydrotrioxide of 2-methyltetrahydrofuran.[24] With increase of temperature, both signals tend to merge and broaden. It has been suggested[28] that this splitting may be caused by the presence of two conformations of the hydrotrioxides of acyclic acetals, which is a result of the non-equivalence of the two oxygen atoms in acetals. The acetal hydroperoxides can be used as effective oxidants for organic compounds. It has been shown[25] that the reaction of 1,1-diethoxyethane hydrotrioxide with diphenylamine and 2,2,6,6-tetramethylpiperidine leads to the formation of the corresponding hydroxy-radicals (the diphenylnitroxy-radical and the 2,6,6,6-tetramethylpiperidin-1-yloxy-radical). Under mild conditions, 1,1-diethoxyethane hydrotrioxide rapidly oxidises pyridine to the *N*-oxide and dipropyl sulphide to dipropyl sulphoxide.[26,27]

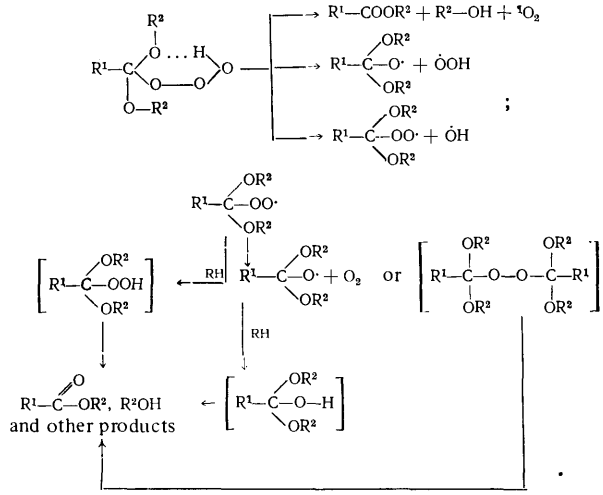
The kinetics of the thermal decomposition of acetal hydroperoxides have been investigated both for the pure substances and for their solutions in diethyl ether and methylene chloride.[17,28] The decomposition follows first-order kinetics. The expressions for the rate constants $k(s^{-1})$ for the thermal decomposition of the hydrotrioxides investigated have the following forms:

$$\begin{array}{ll} \text{(XIX)} & \lg k = 11.8-67.5/\theta, \\ \text{(XX)} & \lg k = 11.1-60.8/\theta, \\ \text{(XXI)} & \lg k = 15.8-79.6/\theta, \\ \text{(XXII)} & \lg k = 12.2-62.3/\theta, \end{array} \qquad \theta = 2.3RT .$$

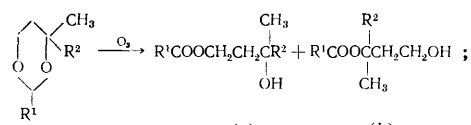
Table 2. The composition of the products of the ozonolysis of 1,3-dioxacyclanes at different temperatures.[29]

Initial compound	Isomer ratio (*a*)/(*b*)		
	−50° C	15° C	50° C
(XXIII)	2:1	2:1	2:1
(XXIV)	2.5:1	2:1	2:1
(XXV)	7:1	3:1	2:1

The low pre-exponential factors for compounds (XIX), (XX), and (XXII) apparently indicate a chain mechanism for the decomposition reaction. All the hydrotrioxides investigated decompose in the temperature range from −40° to +40 °C with formation of singlet oxygen, whose yield (relative to the amount of ozone absorbed) varies from 45 to 80% and depends on the initial compound. In the case of 1,1-diethoxyethane hydrotrioxide (XX), ethyl acetate (0.80–0.85 mole per mole of the ozone absorbed), ethanol (0.70–0.75 mole), water, acetaldehyde, acetic acid, ethyl formate, diethyl carbonate, as well as small amounts of gaseous substances, probably ethane and methane, were detected among the reaction products. The presence of two types of peroxy-compounds, which were not finally identified but are tentatively believed to be an alkyl hydroperoxide and a dialkyl peroxide, was also observed. Apparently the formation of a considerable proportion of ethyl acetate and ethanol together with singlet oxygen is due to the non-radical decomposition of the hydrotrioxide, while the presence of the other two products in the reaction mixture can be accounted for by a free-radical decomposition mechanism:[17]



The reactions of asymmetric 1,3-dioxacyclanes with ozone have been studied in relation to 4-methyl-1,3-dioxan (XXIII), 2,4-dimethyl-1,3-dioxan (XXIV), and 4,4-dimethyl-1,3-dioxan (XXV) in the temperature range from −50° to +50 °C.[29] The reaction products (Table 2) consist of a mixture of the isomeric monoethers (*a*) and (*b*), whose yield relative to the ozone and the substrate which have been consumed reaches 95%:

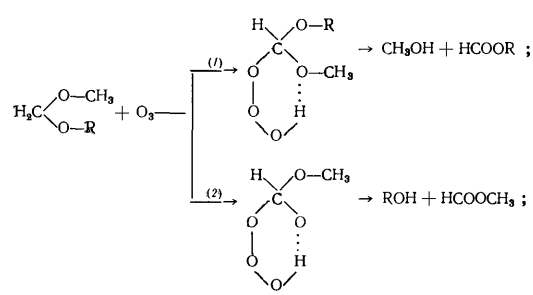


(*a*) (*b*)

R^1, R^2=H (XXIII); R^1=CH_3, R^2=H (XXIV); R^1=H, R^2=CH_3 (XXV) .

In all cases the main products are substances with an acylated primary hydroxy-group (*a*). These results can be accounted for by the preferential dissociation of the C(2)–O(3) bond in the intermediate hydrotrioxide,[29] which is caused by the steric repulsion between the hydrotrioxide group and the axial CH_3 group attached to the C(4) atom in the ring.

The interaction of asymmetric linear acetals with ozone has been studied in relation to methoxyalkoxymethanes at −60 °C.[30] Butyl formate, methyl alcohol, butyl alcohol, and methyl formate accumulate simultaneously in the interaction of ozone with butoxymethoxymethane (XXVI). The ozonolysis of methoxypentoxymethane (XXVII) leads analogously to pentyl formate, methyl alcohol, pentyl alcohol, and methyl formate. The results have been explained within the framework of the following mechanism:



R=C_4H_9 (XXVI), C_5H_{11} (XXVII); (*1*):(*2*)=4:1 .

The observed ratio of pathways (*1*) : (*2*) = 4 : 1 can be explained by the preferential formation of an intramolecular hydrogen bond involving the oxygen atom of the OCH_3 group in the intermediate hydrotrioxide, while the steric hindrance due to the C_4H_9 and C_5H_{11} groups diminishes the probability of the formation of a hydrogen bond involving the OR group.

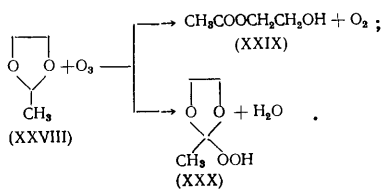
The behaviour of the C–H bond adjoining the three oxygen atoms in relation to ozone has been investigated.[31] Ethyl orthoformate, which is regarded as a derivative of diethoxymethane in which the hydrogen atom has been replaced by the ethoxy-group, was chosen as the object of study. It was established that the main ozonolysis products are diethyl carbonate, ethyl formate, and ethyl alcohol, which accumulate simultaneously:

$$HC(OC_2H_5)_3 + O_3 \begin{cases} \longrightarrow HO_3C(OC_2H_5)_3 \xrightarrow{-O_2} OC(OC_2H_5)_2 + C_2H_5OH \\ \longrightarrow HC(OC_2H_5)_2OCH(O_3H)CH_3 \xrightarrow{-O_2} HCOOC_2H_5 + C_2H_5OH + CH_3CHO \end{cases}.$$

The attack by ozone on the C–H bond adjoining the three oxygen atoms is the main pathway in the process. The reactivity of ethyl orthoformate towards ozone is close to that of diethoxymethane, is twice as high as the reactivity of ethyl alcohol, and is much less than the reactivity of 1,1-diethoxyethane.

III. THE CONTRIBUTION OF RADICAL REACTIONS IN THE OZONOLYSIS OF ACETALS

The results of the ozonolysis of acetals at reduced temperatures (between −78° and 20 °C)[13,29,32,33] clearly demonstrate that the reaction is general and leads to the formation of esters or glycol monoesters with a selectivity not less than 90%. It has been shown[32] that, in the temperature range 20–60 °C, water and organic hydroperoxides, identical to the products obtained in the initiated oxidation of acetals by molecular oxygen, are formed together with the products indicated above. It has also been demonstrated that the reaction of 2-methyl-1,3-dioxolan (XXVIII) with ozone between 20° and 40 °C involves the simultaneous accumulation of the monoester of ethylene glycol (XXIX), the corresponding hydroperoxide (XXX), and water, while at temperatures ≤5° the monoester (XXIX) is virtually the only reaction product (Table 3):



It has also been found[32] that, when 1,1-diethoxyethane (XXXI) is treated with ozone at 20–60 °C, the corresponding hydroperoxide (XXXIII) and water are formed simultaneously with ethyl acetate (XXXII) and ethyl alcohol (Table 3):

$$CH_3CH(OC_2H_5)_2 + O_3 \begin{cases} \longrightarrow CH_3COOC_2H_5 + C_2H_5OH + O_2 \ ; \\ (XXXII) \\ \longrightarrow CH_3C(OOH)(OC_2H_5)_2 + H_2O \ . \\ (XXXIII) \end{cases}$$

With increase of temperature, the yield of the hydroperoxide and water with respect to the ozone consumed increases and at 50–60 °C reaches 30–40%. The presence of considerable amounts of hydroperoxides and water in the products of the ozonolysis of acetals is believed[32–35] to indicate the formation of radicals in the primary reaction of ozone with acetals.

The extent of formation of free radicals in the primary reaction between ozone and acetals has been estimated from the amount of hydroperoxides and water formed and also from the amount of ozone consumed under the conditions of non-chain formation of hydroperoxides.[32] It has been shown that the reactions involving free radicals are more characteristic of linear acetals (~50% at 60 °C), but, with decrease of temperature (<10 °C), the contribution of the radical pathway to the overall process becomes negligible.

Table 3. The influence of temperature on the composition of the products of the reaction of ozone with 1,1-diethoxyethane and 2-methyl-1,3-dioxolan at advanced stages of the reaction in the absence of a solvent.[32]

Reaction temperature, °C	Amount of initial compounds which have reacted, mmol		Yield of products, mmol			
	O_3	acetal	the ester (XXIX) or (XXXII)	C_2H_5OH	the hydroperoxide (XXX) or (XXXIII)	H_2O
			(XXXI)			
60	5.0	11.4	11.1	8.0	1.8	2.1
40	5.0	10.5	10.2	8.2	1.2	2.0
20	10.0	17.5	16.6	14.2	1.7	2.2
5	10.0	12.8	11.8	10.2	0.6	0.7
			(XXVIII)			
40	5.0	10.4	10.0	—	1.3	1.0
20	5.0	6.1	5.7	—	0.9	0.9
5	10.0	10.8	10.6	—	0	0

The rate of formation of free radicals in the reaction of ozone with 1,1-diethoxyethane has been investigated[35] using the results on the liquid-phase chain oxidation of the latter initiated by ozone. With continuous supply of an ozone–oxygen mixture to the reaction mixture, the initial rates of accumulation of the hydroperoxide (v_{AOOH}) and of consumption of ozone (v_{O_3}) were determined (Table 4).

Table 4. The rates of accumulation of the hydroperoxide (XXXIII) (v_{AOOH}), of the consumption of ozone (v_{O_3}), and of initiation (v_i) as a function of the ozone concentration in the gas mixture c_{O_3} in the reaction of ozone with the acetal (XXX) at T = 50 °C.[32,35]

$10^5 c_{O_3}$, M	$10^6 v_{O_3}$, mol litre^{-1} s^{-1}	$10^5 v_{AOOH}$, mol litre^{-1} s^{-1}	$10^6 v_i$, mol litre^{-1} s^{-1}	v_i/v_{O_3}
4.0	2.2	0.7	0.7	0.3
6.6	3.7	1.1	1.3	0.4
11.7	8.5	1.7	3.4	0.4
32.1	23.2	3.3	13.0	0.6
55.8	15.5	2.2	6.0	0.4
84.4	34.6	3.3	13.5	0.4

The rate v_{O_3} is directly proportional to a concentration of ozone in the gas mixture c_{O_3}, while the rates v_{AOOH} vary linearly with $v_{O_3}^{1/2}$ and $v_{AOOH}/v_{O_3} \geq 1$, which agrees with the mechanism of the radical process in which the hydroperoxide

appears in the step involving the abstraction of hydrogen from the substrate by the peroxy-radical:[10]

$$CH_3CH(OC_2H_5)_2 + O_2 \xrightarrow{k_1} CH_3\dot{C}(OC_2H_5)_2,$$
$$CH_3\dot{C}(OC_2H_5)_2 + O_2 \xrightarrow{k_2} CH_3C(O\dot{O})(OC_2H_5)_2,$$
$$CH_3C(O\dot{O})(OC_2H_5)_2 + CH_3CH(OC_2H_5)_2 \xrightarrow{k_3} CH_3C(OOH)(OC_2H_5)_2 + CH_3\dot{C}(OC_2H_5)_2,$$
$$2CH_3C(O\dot{O})(OC_2H_5)_2 \xrightarrow{k_4} \text{non-radical products.}$$

According to the mechanism proposed, the rate of formation of the hydroperoxide AOOH is given by the formula $v_{AOOH} = k_2 k_3^{-1/2}[AH]v_i^{1/2}$, where v_i is the rate of formation of radicals in the system in the stage involving initiation by the reaction of O_3 with the acetal.[35] These results (Table 4) made it possible to determine the ratio v_i/v_{O_3}, characterising the fraction of ozone consumed in the formation of free radicals, which is 0.45 ± 0.15. This permitted the hypothesis that the ozonolysis of acetals takes place simultaneously via molecular and radical pathways:[32,35]

$$CH_3CH(OC_2H_5)_2 + O_3 \text{ (AH)} \begin{cases} \xrightarrow{(a)} CH_3C(O_3H)(OC_2H_5)_2 \xrightarrow{-O_2} CH_3COOC_2H_5 + C_2H_5OH; \\ \xrightarrow{(b)} CH_3\dot{C}(OC_2H_5)_2 + O_2 + \dot{O}H \rightarrow \text{radicals;} \end{cases}$$
$$AH + \dot{O}H \rightarrow \dot{A} + H_2O; \quad \dot{A} + O_2 \rightarrow A\dot{O}_2; \quad A\dot{O}_2 + AH \rightarrow AOOH + \dot{A};$$
$$A\dot{O}_2 + A\dot{O}_2 \rightarrow \text{non-radical products.}$$

At temperatures below 10 °C the fraction of ozone consumed in the formation of free radicals [pathway (*b*)] is negligible and the reaction proceeds almost entirely via the formation of the unstable hydrotrioxide [pathway (*a*)]. With increase of temperature (above 10 °C), the fraction of ozone consumed in the formation of free radicals increases and conditions are created for oxidation by oxygen.

Table 5. The stoichiometry of the reaction of ozone with the dioxolans –R at 0 °C.[36]

R	Amount of acetal mmol		Amount of ozone absorbed, mmol	Solvent	α*
	initial	final			
CH_3	22.8	19.7	3.18	CH_2Cl_2	1.0
	17.4	13.8	3.46	ditto	0.94
	13.6	8.3	5.84	»	1.09
C_6H_5	16.2	11.5	5.00	»	1.06
	12.3	9.4	2.69	»	0.95
	9.2	4.4	4.70	»	1.01
p-$CH_3C_6H_4$	12.3	9.3	2.92	CCl_4	0.92
	9.1	2.6	6.68	ditto	1.03

*α is the ratio of the amount of ozone absorbed and the acetal which has been consumed.

IV. THE INFLUENCE OF THE STRUCTURE OF ACETALS AND THE CONDITIONS IN THEIR REACTION WITH OZONE ON THE RATE OF THE PROCESS

The stoichiometry of the reaction of ozone with acetals was first investigated in relation to 2-phenyl-1,3-dioxolan (I) at −78 °C in methyl acetate.[36] It was established that treatment of one mole of the acetal with ozone results in the formation of one mole of oxygen and one mole of glycol monoester. The results of further studies,[36] carried out in relation to 1,3-dioxolans substituted in 2-position at 0 °C, have shown that the stoichiometric ozone : acetal ratio is close to unity and is almost independent of the initial concentrations of the reactants (Tables 5 and 6).

When the reaction was carried out in the pure substrate (1,1-diethoxyethane or 2-methyl-1,3-dioxan) in the temperature range betwee −20° and 60 °C, it was found[32] that the stoichiometry of the reaction (O_3 : OH) changes from 1 : 1 (between −20° and 0 °C) to 1 : 2 (40–60 °C), which is associated with the occurrence of chain oxidation at temperatures ≥40 °C. On the other hand, when the concentrations of the acetal are close to those of ozone, the stoichiometric ratio of the reactants at 20 °C is close to unity.

Table 6. The stoichiometry of the reaction of ozone with the dioxolans –R in CCl_4 at 0 °C.[36]

R	c_{AH}, 10^{-4} M	c_1, 10^{-4} M	c_2, 10^{-4} M	$\alpha = \frac{c_1 - c_2}{c_{AH}}$
C_6H_5	7.1	9.4	2.3	1.00
	5.0	6.4	1.5	0.98
	3.7	5.8	2.0	1.03
CH_3	5.0	6.0	1.2	0.96
	3.0	6.2	3.3	0.97
	3.0	3.6	0.5	1.03

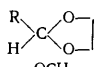
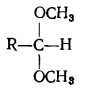
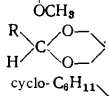
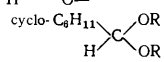
Notation: c_{AH} is the initial concentration of the acetal, c_1 the initial concentration of O_3, c_2 the final concentration of O_3.

This made it possible to investigate the reactivity of acetals with different structures in relation to ozone at 20 °C, the rate of consumption of ozone being followed spectrophotometrically. For all the compounds investigated, the kinetic O_3 consumption curves have the same form and, when [AH] ≫ [O_3], can be satisfactorily represented in a linear form by plotting $\ln [O_3]_0/[O_3]$ against time; under these conditions, ozone is consumed via a pseudounimolecular process with a rate constant $k' = v_{O_3}/[O_3]_0$.[18,29,31–37,40] With increase of the acetal concentration in solution, the rate constant k' increases linearly[32] and the initial rate of consumption of ozone obeys a second-order equation: $v_{O_3} = k[AH][O_3]$; the constant k reflects the overall reactivity of the acetal with respect to ozone and in the temperature range between −78° and 20 °C the process proceeds mainly via the molecular pathway.

The reactivity of 1,3-dioxacyclanes is determined by the ring size and the nature of the substituent at the C(2) carbon atom. The influence of ring size on the reactivity of acetals has been investigated.[18] Comparison of the bimolecular rate constants for the reactions of ozone with five-, seven-, and six-membered 1,3-dioxacyclanes has shown that the reactivity decreases in the sequence 1,3-dioxolan > 1,3-dioxepan > 1,3-dioxan. The dependence of $\lg(k_n/k_0)$ on n, where n (ring size) assumes values of 5, 6, and 7, is analogous to that for the solvolysis of chlorocycloalkanes and the thermal decomposition of cyclic diazoalkanes.[18] This enabled the authors to postulate the appearance in the transition state of a deficiency of electron density at the C(2) atom. The increase of reactivity after the introduction of alkyl and particularly phenyl substituents in the 2-position, which are capable of compensating for the decrease of electron density, has been explained[36] by the stabilisation of the positively charged species produced in which a p_z orbital is formed. The necessary effect is a maximum for 1,3-dioxans, since six-membered rings are less strained, resulting in an intermediate species which has a planar structure with the p_z orbital in

the same plane as the electron pairs of the oxygen atoms and the π orbitals of the phenyl substituent. The transition state in the case of seven- and particularly five-membered 1,3-dioxacyclanes largely deviates from the planar structure, as a result of which the conjugation with the p_z orbital is less effective.

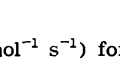
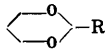
Table 7. Correlation between the rates of reaction with ozone and the Taft substituent constants.

Acetal	Solvent	T, °C	ρ	Correlation coefficient
	CCl_4	0	−1.16	0.995
	C_2H_5OAc	−78	−1.27	0.998
	C_2H_5OAc	−78	−1.58	0.980
	C_2H_5OAc	−78	−1.31	0.910

In order to determine the quantitative relations between the structure of the acetal and its reactivity towards ozone, a study has been made of the influence of substituents on the variation of the rate constants in series differing from one another only in the substituent. The experiments were performed at different temperatures (−78°, 0°, and 20 °C) and in solvents of different polarity (CCl_4,[36,37,40] ethyl acetate[37]).

Taft and Hammett inductive constants have been compared[36] with the relative rate constants for the reaction of ozone with 2-alkyl- or 2-aryl-1,3-dioxolans, which were determined by a competitive method at 0 °C in CCl_4, and also with the pseudo-unimolecular rate constants for the interaction of ozone with 2-alkyl-1,3-dioxans and 1,1-dimethoxyalkanes measured in ethyl acetates at −78 °C. These results showed that electron-donating substituents increase and electron-accepting substituents diminish the reactivity of acetals, the latter increasing by a factor of ~2 following the replacement of a non-polar solvent (hexane) by a polar solvent (ethyl acetate or acetic anhydride). The reaction paramters ρ, the absolute magnitude and sign of which characterises the change in the charge density in the reaction centre on passing from the ground to the transition state, are listed in Table 7. The increase in the negative value of ρ following the replacement of a non-polar solvent (CCl_4) by a more polar solvent (ethyl acetate) is noteworthy.

The quantitative relations between the structure of the acetals and their reactivity in the interaction with ozone in CCl_4 at 20 °C have been investigated taking into account the inductive (σ^*) and steric (E_S) effects of the substituents.[40] For this purpose measurements were made of the rate constants for the reaction of ozone with linear formals and acetals having symmetrical and asymmetric structures, 2-alkyl-1,3-dioxolans and 2-alkyl-1,3-dioxans (Table 8). It has been established that the reactivities of the compounds investigated diminish in the sequence 1,3-dioxolans > 1,3-dioxans > 1,1-dialkoxyalkanes > dialkoxymethanes. The reaction rates constants correlate satisfactorily with the Taft inductive constant σ^*; the sign of ρ is negative and its absolute magnitude varies in the sequence 1.0–1.6 (Table 9). The negative values of ρ in all the examples considered show that a partial positive charge is generated on the acetal carbon atom in the trantision state and the rate of ozonolysis is limited by the hydride transfer stage.[43,44] The characteristic influence of the nature of the solvent on the rate of the process, noted above, confirms the polarity of the transition state. In order to take into account simultaneously the influence of the inductive and steric effects[45] of the substituents

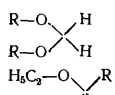
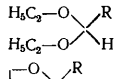
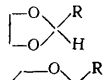
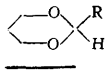
Table 8. The rate constants k (litre mol^{-1} s^{-1}) for reactions of the acetals $H_2C(OR)_2$, $R^1CH(OR^2)(OR^3)$,  , and  with ozone in the liquid phase.[40]

No.	R	k	No.	R^1	k	No.	R^4	k	No.	R^5	k
(XXXIV)	C_2H_5	0.67	(XXVI)	H[a]	0.5	(XXXXV)	H	10.1	(XXXXIX)	H	0.90
(XXXV)	C_3H_7	0.69	(XXXXI)	H[b]	0.42	(XXVIII)	CH_3	22.8	(L)	CH_3	3.91
(XXXVI)	C_4H_9	0.78	(XXXI)	CH_3[c]	3.09	(XXXXVI)	iso-C_3H_7	40.1	(LI)	C_3H_7	9.01
(XXXVII)	iso-C_4H_9	0.91	(XXXXII)	C_3H_7[c]	4.01	(XXXXVII)	C_4H_9	49.2	(LII)	iso-C_3H_7	11.0
(XXXVIII)	C_5H_{11}	1.00	(XXXXIII)	C_4H_9[c]	4.56	(XXXXVIII)	iso-C_4H_9	61.7	(LIII)	C_4H_9	10.5
(XXIX)	iso-C_5H_{11}	0.79	(XXXXIV)	iso-C_3H_7[c]	5.47	(I)	C_6H_5	56.3	(LIV)	C_6H_5	19.5
(XXXX)	cyclo-C_6H_{11}	2.06									

Remarks: 25 °C; solvent—CCl_4; $[O_3] = 1.6 \times 10^{-4}$–$1.6 \times 10^{-3}$ M; [acetal] = 10^{-3}–10^{-2} M; [a] $R^2 = CH_3$, $R^3 = C_4H_9$; [b] $R^2 = CH_3$, $R^3 = iso\text{-}C_5H_{11}$; [c] $R^2 = R^3 = C_2H_5$.

on the rate of ozonolysis of acetals, relations of the type $\lg(k/k_0) = \rho\sigma^* + \delta E_S$ were investigated.[40] The two-parameter correlation (Table 9) describes the best reactivities of the compounds studied. The alkyl substituents R in the alcoholic component of the dialkoxymethanes do not manifest an appreciable steric effect (the steric constant for the reaction series is $\delta = -0.054$) because of their remoteness from the reaction centre, since the reactivities of compounds of this series are mainly determined by the inductive effect of the substituents ($\rho = -2.42$). The reactivities of 1,1-diethoxyalkanes, like those of dialkoxymethanes, are determined mainly by the inductive effect ($\rho = -2.30$). The positive sign of the steric constant δ for this reaction series is noteworthy, indicating a decrease of the reaction rate with increased bulk of the substituent at the reaction centre. The substituents in the reaction series involving the ozonolysis of 2-alkyl-1,3-dioxolans and 2-alkyl-1,3-dioxans (Table 8) exert an appreciable influence on the reactivity.[36,37] Analysis of the constants ρ and δ (Table 9) shows that the rate of the process is determined by the inductive and steric effects of the substituents and that the influence of the latter becomes decisive for 2-alkyl-1,3-dioxans. The observed difference between the five- and six-membered rings can be explained[40] by the conformational characteristics of the molecules considered. It is known that the introduction of a substituent into 1,3-dioxan fixes the chair confirmation,[46] while the C–H bond attacked is in a conformation favourable for reaction because its orientation is antiperiplanar relative to the orbitals of the free electron pairs of the oxygen atoms.[20] The five-membered ring does not have quite such a distinct conformational minimum[47,48] and the steric influence of the substituents in the 2-position is therefore smaller.

Table 9. The inductive (ρ) and steric (δ) constants for the reaction series involving the reaction of ozone with acetals.[40]

Compound	$\lg(k/k_0) = \rho\sigma^*$		$\lg(k/k_0) = \rho\sigma^* + \delta E_S$			
	ρ	r	ρ	δ	r	s
	−1.55	0.973	−2.42	−0.054	0.975	$0.4 \cdot 10^{-2}$
	−1.32	0.991	−2.30	0.38	0.998	$2.6 \cdot 10^{-4}$
	−1.02	0.937	0.68	−0.58	0.992	$0.4 \cdot 10^{-2}$
	−1.6	0.994	5.89	−2.92	0.990	$1.6 \cdot 10^{-2}$

Notation: r is the correlation coefficient and s the variance.

The activation parameters for the ozonolysis of linear and cyclic acetals determined in two investigations[36,37] are listed in Table 10. The high negative entropies of activation $\Delta S^{\neq}$ ($\Delta S^{\neq} = -141$ to -106 J mol^{-1} K^{-1} [36]) and the anomalous relation between the reactivities of linear acetals and the corresponding enthalpies of activation, namely the fact that the increase of the reactivity of the acetal is accompanied by an increase of the enthalpy of activation,[37] are noteworthy. It has also been established[37] that the enthalpy of activation $\Delta H^{\neq}$ and the entropy of activation $\Delta S^{\neq}$ are linked by a linear relation, so that a compensation effect is observed ($\Delta H^{\neq} = \beta\Delta S^{\neq} + h_0$; β is the isokinetic temperature and h_0 is a constant).[37] For linear acetals, the isokinetic temperature is much below the experimental temperature range and the reactivity is determined by the entropy factor.[37] Since, according to Deslongchamps et al.[22], linear acetals exist in a conformation which is inert towards ozone, in order to become reactive the acetal molecules must assume a favourable conformation[20] in which the C–H bond attacked is oriented antiperiplanarly relative to the unshared electron pairs of the oxygen atoms. For cyclic acetals, which exist in a favourable conformation,[22] β lies at higher temperatures than the working range[37] and the enthalpy factor determines the reactivity.

V. THE MECHANISM OF THE INTERACTION OF OZONE WITH ACETALS

The reaction of ozone with a saturated C–H bond can proceed via homolytic, concerted, and heterolytic mechanisms.[36,49,50]

The homolytic mechanism can operate in principle in several ways.[50] It can involve a chain reaction initiated by oxygen atoms, which are formed on reversible dissociation of ozone:

$$O_3 \rightleftarrows O_2 + O \quad (\Delta H = 107 \text{ kJ mol}^{-1} \text{ (Ref.50)}).$$

Analysis by Denisov[50] indicated a low probability of the occurrence of the chain reaction at reduced temperatures. This agrees with the finding that the initiating effect of ozone on the gas-phase oxidation of hydrocarbons is observed only at temperatures above 100 °C, where ozone decomposes at an appreciable rate.[50] In the liquid phase at moderate temperatures the radicals can be generated via a bimolecular reaction. However, the mechanism involving abstraction of a hydrogen atom is believed to be unlikely in view of the high endothermicity of the reaction:

$$RH + O_3 \rightarrow R^{\cdot} + HO_3^{\cdot} - q \quad (q = Q_{R-H} - 255 \text{ [56]}),$$

which does not agree with experimental data.[36] For example, $Q_{R-H} \cong 340$ kJ mol^{-1} [10] and $q \cong 85$ kJ mol^{-1} for 1,3-dioxacyclanes, while the activation energy for the ozonolysis of acetals varies in the range 22–35 kJ mol^{-1}.[36]

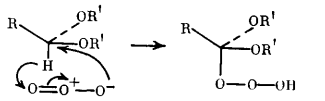
The formation of radicals is a result of the attack by ozone on the C and H atoms in the C–H bond, while the mechanisms $RH + O_3 \rightarrow R\dot{O} + H\dot{O}_2$ [54,55] and $RH + O_3 \rightarrow R\dot{O}_2 + H\dot{O}$ [57,58] are also unlikely, because it is known that this should lead to a high activation energy (above 100 kJ mol^{-1}) and to a high negative entropy of activation. Denisov pointed out[50] that the reaction

$$RH + O_3 \rightarrow R^{\cdot} + HO^{\cdot} + O_2 - q \quad (q = Q_{R-H} - 320 \text{ kJ mol}^{-1} \text{ (Refs.59, 60)})$$

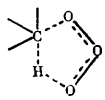
is thermodynamically the most favourable among homolytic reactions. For example, the endothermicity of this reaction for 1,3-dioxacyclanes is only 20 kJ mol^{-1}, which agrees well with the activation energy $E = 22$–35 kJ mol^{-1} [36] (for endothermic reactions, $E > |q|$ [50]). The above analysis shows that the homolytic interaction of ozone with a saturated C–H bond can proceed at the experimentally observed rate at elevated temperatures, provided that the energy of the C–H bond attacked does not exceed 340 kJ mol^{-1}. This is consistent with the finding that, under conditions suitable for a chain reaction, namely [RH] > 5 M and $T > 50$ °C, ozone initiates the chain oxidation of acetals.[32,35] Below 0 °C, the probability of the formation of free radicals as a result of the primary reaction of ozone with acetals is low.

The observed high rates of reaction of ozone with acetals at reduced temperatures (Table 1) indicate the possibility of the concerted and heterolytic reaction mechanisms.

The concerted mechanism involving the 1,3-dipolar insertion of ozone in the C–H bond with formation of an intermediate hydrotrioxide can be represented by the following scheme accordingly to Nagia and Benson:[49]



In the case of a concerted reaction, the insertion of O_3 in the C–H bond takes place tentatively via a five-membered cyclic transition state of the following form:[49]



Calculations have shown that the formation of the cyclic transition state, involving a marked extension of the C–H bond and a considerable change in the O–O–O valence angle in the ozone molecule, leads to a high activation energy (above 100 kJ mol^{-1}) [51] and to a high negative entropy of activation.[50] Consequently the mechanism involving the 1,3-dipolar insertion of ozone is also unlikely.

The primary reaction of ozone with an acetal apparently takes place heterolytically via the transfer of a hydride ion to the O_3 molecule with formation of a close ion pair in a solvent cage, which then recombines to form the hydrotrioxide:[36,49]

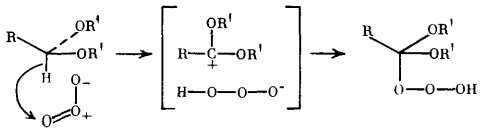
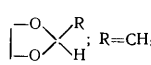
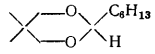


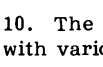
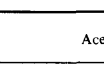
Table 10. The activation parameters for the reactions of ozone with various acetals.

No.	Acetal	Solvent	$\Delta H^{\neq}$, kJ mol^{-1}	$\Delta S^{\neq}$, J mol^{-1} K^{-1}
(XXVIII)	 R=CH_3	CCl_4	22.6±2.9	−141±10
(I)	R=C_6H_5	CCl_4	24.9±0.4	−125±2
(III)		Hexane	34.3±3.5	−106±17
(III)	ditto	C_2H_5OAc	33.2±2.5	−106±12
(LV)	iso-C_3H_7–C(OCH$_3$)(OCH$_3$)–H	C_2H_5OAc	37.4±0.7	−110±3
(VII)	C_6H_{17}–C(OCH$_3$)(OCH$_3$)–H	C_2H_5OAc	35.2±1.6	−121±7

Under these conditions, a partial positive charge is generated on the acetal carbon atom in the transition state. The validity of this hypothesis is confirmed by the results of a study of the reactivity of acetals using the Taft correlation equation (Table 9),[36,40] the study of the influence of the ring size and of the nature of the substituent at the acetal carbon atom on the reactivity of acetals,[18] and the high negative activation entropies $\Delta S^{\neq}$ for the ozonolysis of acetals (Table 10).[36] It is known[52] that the appearance of a pair of charges in the transition state leads to a significant decrease of the entropy and $\Delta S^{\neq}$ can reach −120 J mol^{-1} K^{-1}.[52] The results of Benson's thermochemical calculations[49] support the heterolytic reaction pathway.

Additional data concerning the primary reaction of ozone with acetals have been obtained in a study of the kinetic isotope effect (KIE).[53] Experiments on the reaction of ozone with the deuterio-acetals of acetaldehyde, benzaldehyde, and formaldehyde demonstrate unambiguously that in acetals the attack by ozone is directed to the C–H bond adjoining two heteroatoms (Table 11). Estimation of the absolute values of the KIE and their comparison with the known $\Delta S^{\neq}$ for the corresponding acetals[36] make it possible to infer the degree of charge separation in the transition state. Since the KIE is manifested when the hydride ion has been partially transferred to the ozone molecule in the transition state, its magnitude increases with increase of the degree of transfer and reaches its maximum value ($k_H/k_D \cong 6.9$ at 25 °C [52]) for complete symmetry of the transition state when the C–H bond ruptured and the H–O bond formed have similar strengths.[52] Consequently, the increase of the KIE on passing from formals and linear acetals to cyclic acetals (Table 11), accompanied by a decrease of the corresponding $\Delta S^{\neq}$, indicates an increase in the degree if charge separation in the transition state of the reaction between acetals and ozone.

Table 11. The kinetic isotope effects and entropies of activation in the reactions of ozone with acetals at 20 °C [53] ($v_{O_3} = kc_{ac}c_{O_3}$).

Compound	k, litre mol^{-1} s^{-1}		k_H/k_D	$\Delta S^{\neq}$, J mol^{-1} K^{-1} (X = H)
	X=H	X=D		
	22.8	4.8	4.9	−141
	53.6	12.4	4.3	−125
$CX_3CX(OC_3H_7)_2$	2.0	0.55	3.6	−104
	1.3	0.4	3.0	−94.3
	5.6	1.9	2.9	—
$X_2C(OC_3H_7)_2$	0.60	0.28	2.1	—

Thus analysis of data on the composition of the products of the reactions of ozone with acetals,[20,29,32] the stoichiometry of the reaction,[32,36] and the influence of the nature of the substituents and the structure of the acetals on their reactivity over a wide temperature range (between −78° and 60 °C),[18,40] allowance for the polarity of the medium,[37] and analysis of the activation parameters for the process and of the KIE [36,53] permit the conclusion that the nature of the primary reaction of ozone with acetals is complex. At reduced temperatures the process proceeds via a heterolytic mechanism with transfer of the hydride ion and the formation of an ion pair in a solvent cage: its recombination leads to an intermediate highly unstable hydrotrioxide whose decomposition leads to the formation of the observed reaction products.

Under these conditions (between −70° and 20 °C), the probability of the homolytic reaction pathway is insignificant. With increase of temperature (>20 °C), the fraction of ozone consumed in the formation of free radicals increases, reaching ~40–50% at 50 °C.[32,35]

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Thioalkylation Reactions

V.I.Dronov and Yu.E.Nikitin

A systematic account is given of data on thioalkylation reactions—reactions involving the substitution of mobile hydrogen atoms by an alkylthiomethyl (or another alkylthioalkyl) group on treatment with formaldehyde (or other aldehydes) and a thiol.
The bibliography includes 51 references.

CONTENTS

I. Introduction 554
II. Thioalkylation reactions 554

I. INTRODUCTION

The aminomethylation reaction (the Mannich reaction) is widely known and has been described in detail in reviews and monographs.[1-6] It consists of the treatment of certain compounds containing mobile protons (ketones, phenols, various heterocycles, etc.) with formaldehyde and primary or secondary amines (or ammonia) whereby it is possible to introduce the alkylaminomethyl group into such compounds:

$$RH + CH_2O + HN\!\!\!\diagup\!\!\!\diagdown \rightarrow RCH_2N\!\!\!\diagup\!\!\!\diagdown + H_2O .$$

In the course of the investigation of the condensation of ketones with formaldehyde and thiols, we introduced the term "thioalkylation" for this reaction by analogy with the Mannich reaction.[7] We include among thioalkylation reactions all those in which treatment of compounds having mobile protons with formaldehyde (or other aldehydes) and a thiol results in the substitution of these protons by an alkylthiomethyl (or another alkylthioalkyl) group:

$$RH + CH_2O + R'SH \rightarrow RCH_2SR' + H_2O .$$

These reactions are analogues of the Mannich reaction and constitute a special case of the more general thiomethylation reaction [sic (Ed.of Translation)].[8]

A series of such reactions have been described in the literature long before we investigated the thioalkylation of ketones. In this communication we give a systematic account of such reactions and have combined them under a common name (such combination without taking into account the reaction mechanism is to some extent rather formal).

II. THIOALKYLATION REACTIONS

1. Thioalkylation of ammonia and amines

The familiar reaction involving the aminomethylation of thiols can be formally regarded as thioalkylation in which amines or ammonia function as compounds with mobile protons:

$$R_2NH + CH_2O + R'SH \rightarrow R_2NCH_2SR' + H_2O .$$

Since this reaction has been described in the literature only very briefly,[6] we decided to carry out a more detailed survey.

Tris(arylthiomethyl)amines were obtained for the first time[9] by refluxing arenethiols and hexamethylenetetramine in anhydrous dioxan in a nitrogen atmosphere (toluene-α-thiol reacts analogously):

$$(CH_2)_6N_4 + 6RSH \rightarrow 2N(CH_2SR)_3 + 2NH_3 ;$$
$$R=C_6H_5,\ p\text{-}BrC_6H_4,\ p\text{-}O_2NC_6H_4,\ p\text{-}CH_3C_6H_4,\ C_6H_5CH_2 .$$

The attempt to obtain tris(pentylthiomethyl)amines by this procedure was unsuccessful.

Analogous results have been obtained[10] on refluxing (for 15–30 min) arenethiol (or toluene-α-thiol), a 37% solution of formaldehyde, and aqueous ammonia (in molar proportions of 3 : 3 : 1) in alcohols. The reaction with benzenethiol was carried out for 2 h without heating:

$$NH_3 + 3CH_2O + 3RSH \rightarrow N(CH_2SR)_3 + 3H_2O ;$$
$$R=C_6H_5;\quad p\text{-}t\text{-}C_4H_9C_6H_4;\ p\text{-}ClC_6H_4;\ m\text{-}CH_3C_6H_4;\ p\text{-}O_2NC_6H_4;\ 2,4,6\text{-}(CH_3)_3C_6H_2;$$
$$2\text{-}C_{10}H_7;\ C_6H_5CH_2 .$$

The yields of tris(arylthiomethyl)amines were 21.5–80.5%.

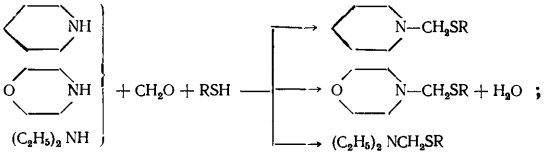
Bis(ethylthiomethyl)amine was synthesised by the reaction of ammonium chloride, a 37% aqueous solution of formaldehyde, and ethanethiol in molar proportions of 3.96 : 9.87 : 6.46 at pH < 6 and subsequent treatment of the reaction mixture with an excess of a dilute solution of sodium hydroxide.[11]

The thioalkylation of amines was first described by McLeod and Robinson.[12] The reaction of diethylamine with 35% aqueous formaldehyde solution and ethanethiol afforded diethyl(ethylthiomethyl)amine in 53% yield:

$$(C_2H_5)_2NH + CH_2O + C_2H_5SH \rightarrow (C_2H_5)_2NCH_2SC_2H_5 + H_2O .$$

Diethyl(isopropylthiomethyl)amine was obtained analogously.

A more detailed study of the thioalkylation of secondary aliphatic amines showed[13] that, in contrast to phenols, the reaction of arenethiols with formaldehyde and secondary aliphatic amines results in the formation of aryl dialkylaminomethyl sulphides and not Mannich bases. Thus a series of aryl piperidinomethyl, aryl morpholinomethyl, or aryl diethylaminomethyl sulphides have been obtained from the corresponding amines, aqueous formaldehyde, and various arenethiols:



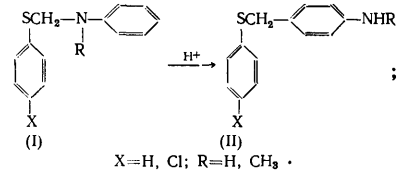
$$R=C_6H_5;\ o\text{-}CH_3C_6H_4;\ m\text{-}CH_3C_6H_4;\ 2\text{-}C_{10}H_7;\ 1\text{-}C_{10}H_7;\ p\text{-}O_2NC_6H_4;\ p\text{-}ClC_6H_4;$$
$$p\text{-}BrC_6H_4;\ 2,5\text{-}Br_2C_6H_3;\ p\text{-}CH_3OC_6H_4;\ 2,4,6\text{-}(CH_3)_3C_6H_2 .$$

The secondary amine was added to an equimolar amount of the arenethiol at a temperature not exceeding 20 °C and the mixture was then treated with an equimolar amount of aqueous formaldehyde (37%), the mixture was heated to 80 °C, and was maintained at this temperature for 2 h. The yields were 22–89% of aryl piperidinomethyl sulphides, 33–96% of aryl morpholinomethyl sulphides, and 31–71% of aryl diethylaminomethyl sulphides.

The thioalkylation of secondary aliphatic amines has been investigated[14] and it has been established that, when a solution of 0.1 mole of an arenethiol, 0.1 mole of aryl methylamine, and 0.10–0.17 mole of a 35–40% aqueous solution of formaldehyde are heated in 20 ml of alcohol at 80 °C for 2 h, *N*-aryl-*N*-methylaminomethyl sulphides are obtained in 66–93% yield:

$$R'NHCH_3 + CH_2O + R^2SH \rightarrow R'(CH_3)NCH_2SR^2 + H_2O;$$
$$R' = C_6H_5;\ R^2 = C_6H_5,\ p\text{-}ClC_6H_4;\ 2,4,6\text{-}(CH_3)_3C_6H_2;\ C_6Cl_5;$$
$$R' = p\text{-}O_2NC_6H_4;\ R^2 = p\text{-}ClC_6H_4;\ R' = p\text{-}CH_3OC_6H_4;\ R^2 = p\text{-}ClC_6H_4.$$

The aryl *N*-arylthiomethyl sulphides (I), obtained by the thioalkylation of aromatic amines in the presence of strong acids, readily rearrange in high yields into the isomeric aryl *p*-aminobenzylsulphides (II):[14]

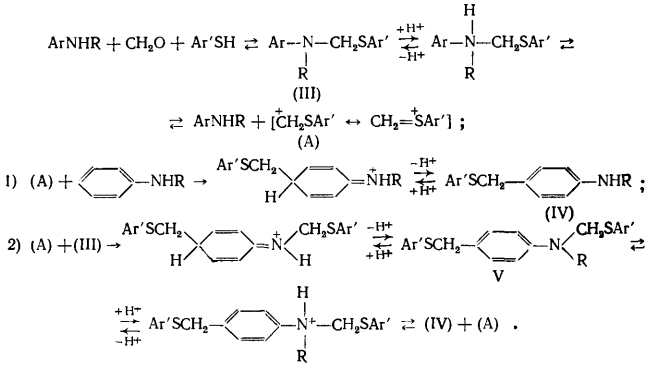


(I) (II)

X=H, Cl; R=H, CH_3.

In order to obtain compound (II), the sulphide (I) is refluxed with an equimolar amount of concentrated hydrochloric acid in 95% alcohol. Under analogous conditions, the sulphides (II) can be obtained in one stage by condensing aromatic amines and thiols with formaldehyde in the presence of strong acids (HCl, HBr, H_2SO_4). The aromatic thiols employed were C_6H_5SH, $p\text{-}ClC_6H_4SH$, $p\text{-}CH_3C_6H_4SH$, $p\text{-}O_2NC_6H_4SH$, and 2,4-$(CH_3)_3C_6H_2SH$, while the aromatic amines were $C_6H_5NH_2$, $2\text{-}C_{10}H_7NH_2$, $m\text{-}ClC_6H_4NH_2$, $p\text{-}CH_3C_6H_4NH_2$, and *N*-methylaniline. The yields of the products were 39–90%.

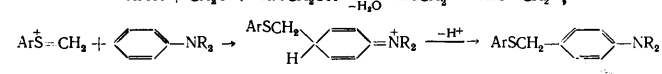
The mechanism of this reaction evidently involves the protonation of aryl *N*-alkyl-*N*-arylaminomethyl sulphide (III) at the nitrogen atom and subsequent decomposition into the initial amine and the resonance-stabilised carbonium-sulphonium ions (A).[16] The latter can then alkylate either the alkylarylamine or the sulphide (III); in the former case *N*-alkyl-*p*-aminobenzyl aryl sulphide(IV) is formed immediately after deprotonation while in the latter the intermediate *N*-alkyl-*N*-arylthiomethyl-*p*-aminobenzyl aryl sulphide (V) is produced and is then converted into the aryl benzyl sulphide (IV) with regeneration of the ion (A):



The second hypothesis is supported by the fact that the intermediate (V) can be isolated in a satisfactory yield when the reaction of *p*-chlorobenzenethiol and formaldehyde with *N*-methylamine is carried out in the presence of concentrated hydrochloric acid at 40 °C; this product is fully converted into the sulphide (IV) on raising the temperature to 80 °C. This mechanism is also confirmed by the finding that the *ortho*-product of the condensation reaction was not obtained even in those cases where the *p*-position in the aromatic amine is occupied (with the exception of the reaction with $2\text{-}C_{10}H_7NH_2$ [15]); it has been noted that the large size of the arylthiomethyl group prevents the entry of the substituent into the *ortho*-position.

Apart from the primary and secondary amines, tertiary aromatic amines also enter into the reaction described above, but the yields of products are then low (15–33%):[16]

The mechanism involving the intermediate formation of arylthiomethanol, whose protonation and subsequent elimination of the water molecule yield a carbonium-sulphonium ion, has been proposed for this reaction. The ion reacts with an arylamine to form aryl *NN*-dialkyl-*p*-aminobenzyl sulphide:[16]



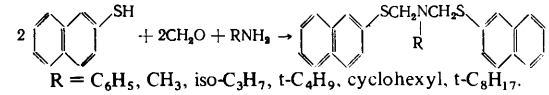
A study of the thioalkylation of primary aromatic amines[14] established that, in contrast to primary aliphatic amines and benzylamines, which usually give rise to a mixture of secondary and tertiary amines via the Mannich reaction, aromatic amines condense with arenethiols and formaldehyde (in molar proportions of 1 : 1 : 1) to form almost exclusively aryl *N*-arylaminomethyl sulphides:

$$RNH_2 + CH_2O + R'SH \rightarrow RNHCH_2SR' + H_2O$$
$$R = C_6H_5;\ R' = C_6H_5;\ p\text{-}ClC_6H_4;\ 2,4,6\text{-}(CH_3)_3C_6H_2;\ R' = p\text{-}ClC_6H_4;$$
$$R\ m\text{-}ClC_6H_4;\ p\text{-}ClC_6H_4;\ p\text{-}CH_3OC_6H_4;\ p\text{-}O_2NC_6H_4.$$

The yields of the reaction products are 16–86%, when the thiol : amine : formaldehyde molar ratios are 2 : 1 : 2, 1,3,5-triaryl-1,5-dithia-2-azapentanes are obtained:

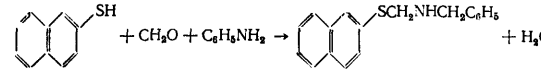
$$RNH_2 + 2CH_2O + 2R'SH \rightarrow R'SCH_2{-}\underset{\displaystyle R}{N}{-}CH_2SR' + 2H_2O;$$
$$R' = C_6H_5,\ R = C_6H_5,\ p\text{-}ClC_6H_4.$$

The thioalkylation of various aliphatic amines with naphthalene-2-thiol and formaldehyde in molar proportions of 1 : 2 : 2 (in ethyl acetate at 25–28 °C for 48 h) leads to analogous results:[17,18]



R = C_6H_5, CH_3, iso-C_3H_7, t-C_4H_9, cyclohexyl, t-C_8H_{17}.

The yields of the reaction products are 55–95%. The condensation of naphthalene-2-thiol, formaldehyde, and benzylamine also yielded benzylaminomethyl-2-naphthyl sulphide:



The following reaction mechanism has been proposed:[18]

$$C_{10}H_7SH \rightleftarrows C_{10}H_7S^- + H^+;$$
$$RNH_2 + CH_2O \rightarrow RNHCH_2OH;$$
$$RNHCH_2OH + H^+ \rightarrow RNHCH_2^+ \leftrightarrow R\overset{+}{N}H{=}CH_2;$$
$$C_{10}H_7S^- + R\overset{+}{N}H{=}CH_2 \rightarrow C_{10}H_7SCH_2NHR;$$
$$C_{10}H_7SCH_2NHR + CH_2O \rightarrow C_{10}H_7SCH_2{-}\underset{\displaystyle R}{N}{-}CH_2OH \text{ etc.} \rightarrow C_{10}H_7SCH_2{-}\underset{\displaystyle R}{N}{-}CH_2SC_{10}H_7.$$

2. Thioalkylation of Hydrogen Halides

The familiar reaction involving the chloromethylation of thiols can be regarded as a thiomethylation reaction in which hydrogen chloride behaves as a compound with a mobile proton:

$$HCl + CH_2O + RSH \rightleftarrows RSCH_2Cl + H_2O.$$

Böhme[19] obtained chloromethyl ethyl sulphide by this reaction for the first time by passing hydrogen chlorides into a mixture of ethanethiol and paraformaldehyde cooled to −15 °C:

$$n\,C_2H_5SH + (CH_2O)_n + n\,HCl \rightleftarrows n\,C_2H_5SCH_2Cl + n\,H_2O.$$

Alkyl and aryl chloromethyl sulphides $RSCH_2Cl$, where R = CH_3,[20,22] C_2H_5,[19,22,26] C_3H_7,[20,22] iso-C_3H_7,[22] n-C_4H_9, iso-C_4H_9, s-C_4H_9, t-C_4H_9, n-C_5H_{11}, s-C_5H_{11},[22,23] C_6H_{13},[22,28] 2-ethylbutyl, 1-methylheptyl,[23] C_8H_{17},[28,29] $C_{12}H_{25}$, $C_{14}H_{20}$,[28] cyclohexyl,[22] C_6H_5, p-ClC_6H_4, or $C_6H_5CH_2$ [20] having different structures were subsequently obtained with the aid of this procedure. The yields of alkyl chloromethyl sulphides are 43–85%.

When paraldehyde was used instead of paraformaldehyde, a series of alkyl and aryl α-chloroethyl sulphides were obtained:

$$3RSH + (CH_3CHO)_3 + 3HCl \rightleftarrows 3RSCHCl + 3H_2O;$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad CH_3$$

R = CH_3 (Refs.20, 21), C_2H_5 (Refs.20–22, 24, 26), t-C_4H_9 (Ref.27), C_6H_5 (Ref.21), iso-C_3H_7 (Refs.22, 24), alkyl (Refs.24, 25), C_4H_9, C_5H_{11} (Refs.22, 24).

The yields of the products are 30–90%.

Other aldehydes have also been used:

$$RSH + R'CHO + HCl \rightleftarrows RSCHCl + H_2O;$$
$$\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\qquad\quad R'$$

R = CH_3, R′ = C_6H_5 (Ref.20); R = R′ = C_2H_5 (Ref.21); R = C_2H_5, R′ = n-C_3H_7, iso-C_3H_7, C_6H_5 (Ref.26).

The yields of the α-chloroalkyl sulphides in these syntheses are 40–81%.

In one investigation acetone was used in the thioalkylation of hydrogen chloride instead of an aldehyde and α-chloroisopropyl ethyl sulphide was then obtained in 20% yield:

$$C_2H_5SH + CH_3COCH_3 + HCl \rightleftarrows CH_3C(Cl)SC_2H_5 + H_2O.$$
$$\qquad\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\qquad\qquad\quad CH_3$$

The thioalkylation of hydrogen chloride in a solvent (CH_2Cl_2) using anhydrous calcium or magnesium sulphate to absorb the water formed in the reaction[30] did not result in an increase of the yield of the required product. The yields were 50% of $C_2H_5SCH_2Cl$, 63% of iso-$C_3H_7SCH_2Cl$, and 45% of $CH_3SCH(Cl)CH_3$. In the syntheses by Böhme's method the yields are 43–60% of the first product,[19,20,22,26] 85% of the second product,[22] and 30–59% of the third product.[20,21]

In the thioalkylation of hydrogen chloride in benzene[28,31] the yields of alkyl chloromethyl sulphide are independent of the length of the hydrocarbon group in the thiol and depend mainly on the reaction temperature and the amount of solvent employed. The highest yields (>70%) are reached at 0–10 °C when CH_2O and RSH are employed in molar proportions of 1.2 : 1 (the benzene : thiol ratio is 4.5 : 1).

There has been one study on the thioalkylation of hydrogen bromide[20] in which bromomethyl ethyl sulphide was obtained by Böhme's method in 44% yield.

The data on the mechanism of the thioalkylation of *NN*-dialkylanilines suggest the following most probable mechanism of the thioalkylation of hydrogen halides:

$$RSH + CH_2O \rightleftarrows RSCH_2OH;$$
$$HX \rightleftarrows H^+ + X^-;$$
$$RSCH_2OH + H^+ \rightarrow RSCH_2\overset{+}{O}H_2 \xrightarrow{-H_2O} RSCH_2^+ \leftrightarrow R\overset{+}{S}{=}CH_2;$$
$$RSCH_2^+ + X^- \rightarrow RSCH_2X;$$
$$X = Cl, Br.$$

3. Thioalkylation of Ketones

The thioalkylation of ketones was investigated for the first time by the authors of the present review.[32] It was established[33] that the reaction proceeds readily in the presence of alkalis; calcium carbonate weakly catalyses the reaction, while triethylamine has no catalytic effect. When piperidine is added to a mixture of a ketone, a thiol, and formaldehyde, *N*-alkylthiomethylpiperidine is formed but does not catalyse the reaction. The reaction in the presence of alkalies is exothermic and in many cases reaches completion very rapidly at room temperature. In the remaining instances heating of the mixture to 50 °C is sufficient to complete the reaction.

Aliphatic, cyclic, and aliphatic-aromatic ketones and all thiols other than aromatic thiols enter into the thioalkylation reaction. The methylene group adjoining the carbonyl group in alkyl methyl ketone is the most reactive.

When a fivefold excess of the ketone is treated with equimolar amounts of a thiol, formaldehyde, and sodium hydroxide, mono(alkylthiomethyl)-substituted ketones are obtained:[7,33,34]

$$R^1COCH_2R^2 + CH_2O + R^3SH \rightarrow R'COCH(R^2)CH_2SR^3 + H_2O;$$
$R^1{=}R^2{=}CH_3$; $R^3{=}C_2H_5$; n-C_4H_9; t-C_4H_9; C_8H_{17}, cyclohexyl; $C_6H_5CH_2$; $R^1{=}CH_3$; $R^2{=}C_3H_7$; $R^3{=}C_4H_9$; $R'{=}C_6H_5$, $R^2{=}CH_3$, $R^3{=}C_6H_5$, n-C_4H_9, t-C_4H_9, cyclohexyl; $R^1R^2{=}(CH_2)_4$; R^3-n-C_4H_9; t-C_4H_9; cyclohexyl; $R^1{=}CH_3$; $R^2{=}H$; $R^3{=}C_4H_9$; $R'{=}C_6H_5$; $R^2{=}H$; $R^3{=}C_4H_9$, C_8H_{17}.

The yields of the reaction products are 50.2–100%.

When equimolar amounts of acetone, butanethiol, formaldehyde, and sodium hydroxide interact, 61% of bis(butylthiomethyl)acetone and only 10.5% of mono(butylthiomethyl)acetone are obtained. The reaction involving acetophenone produces analogously under these conditions 64.2% of bis(butylthiomethyl)acetophenone and 25.9% of the mono-(butylthiomethyl) derivative.[35] This can be explained by the fact that the methylene group, which is more reactive than the methyl group, appears next to the carbonyl group in the mono(butylthiomethyl) derivatives formed:

$$CH_3COCH_3 + CH_2O + C_4H_9SH \rightarrow CH_3COCH_2CH_2SC_4H_9 + H_2O;$$
$$CH_3COCH_2CH_2SC_4H_9 + CH_2O + C_4H_9SH \rightarrow CH_3COCH(CH_2SC_4H_9)_2 + H_2O.$$

When ketones were allowed to react with twice the molar amounts of a thiol, formaldehyde, and sodium hydroxide in an aqueous alcoholic medium at 20–50 °C, bis(alkylthiomethyl)-substituted ketones were obtained in 38–93% yields:[33,35]

$$R^1COCH_2R^2 + 2\,CH_2O + 2\,R^3SH \rightarrow R^1COC(R^2)(CH_2SR^3)_2 + 2\,H_2O;$$
$R^1{=}CH_3$; $R^2{=}H$; $R^3{=}C_2H_5$; C_4H_9; $R^1{=}C_6H_5$; $R^2{=}H$; $R^3{=}C_2H_5$; C_4H_9; C_6H_{13}; cyclohexyl; $C_6H_5CH_2$; $R^1R^2{=}(CH_2)_3CH$; $R^3{=}C_4H_9$.

It is noteworthy that the introduction of the first $RSCH_2$ group into the ketone molecule, with the exception of acetone and acetophenone, takes place readily, while the introduction of the second $RSCH_2$ group is difficult. This fact is manifested particularly clearly in the thioalkylation of cyclohexanone with butanethiol. The introduction of the

first $C_4H_9SCH_2$ group into the cyclohexanone molecule proceeds via an exothermic reaction and is completed in 2 h, while the introduction of the second $C_4H_9SCH_2$ group requires prolonged (10 h) heating at 50 °C.[35]

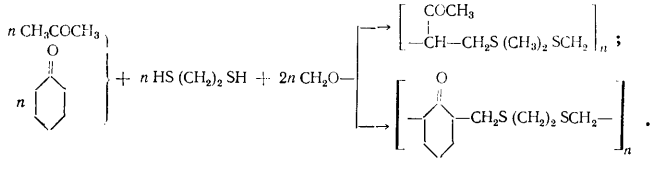
When butanone is thioalkylated with two moles of butanethiol and formaldehyde, 1,3-bis(butylthiomethyl)-2-butanone is obtained, while the reaction with three moles of ethanethiol and formaldehyde gives rise to 1,3,3-tris(ethylthiomethyl)-2-butanone. The third $C_2H_5SCH_2$ group enters the sterically more hindered 3-position rather than the 1-position.[35]

The thioalkylation of acetone by four moles of a thiol, formaldehyde, and sodium hydroxide results in the formation of 1,1,3,3-tetrakis(alkylthiomethyl)-2-propanones:[33]

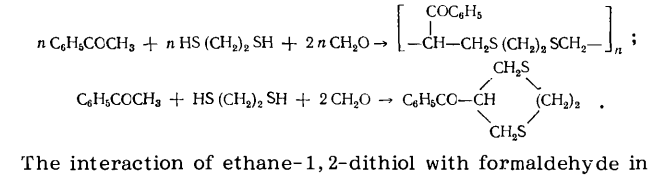
$$CH_3COCH_3 + 4CH_2O + 4RSH \rightarrow (RSCH_2)_2CHCOCH(CH_2SR)_2 + 4H_2O;$$
$$R = C_2H_5;\ C_4H_9;\ C_6H_{11};\ C_{12}H_{25};\quad t\text{-}C_{12}H_{25};\ \text{cyclohexyl},\ C_6H_5CH_2\ .$$

The yields of the required products are 77–93%.

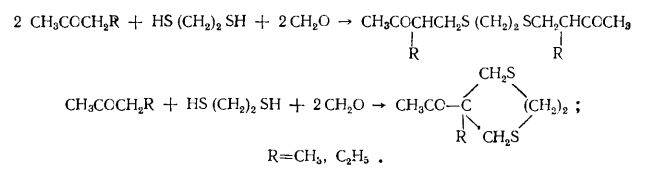
The thioalkylation of ketones by dihydric thiols, particularly by ethane-1,2-dithiol, has been investigated.[36] The condensation of acetone and cyclohexanone with formaldehyde and ethane-1,2-dithiol in molar proportions of 1 : 2 and 4 : 1 in the presence of alkali at room temperature gives rise to polymeric ketobis-sulphides in yields of 92.2 and 94% respectively:



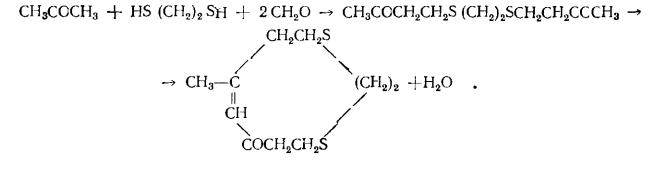
The yield of the polymeric ketobis-sulphides obtained from acetophenone under these conditions is 16.7% and the main reaction product is 6-benzoyl-1,4-dithiacycloheptane (71.4%):[36]



The interaction of ethane-1,2-dithiol with formaldehyde in molar proportions of 1 : 2.4 with a 20-fold excess of butanone or 2-pentanone at 20 °C in the presence of alkali yields 3,10-dimethyl- and 3,10-diethyl-5,8-dithiadodecane-2,11-diones respectively together with small amounts of 6-methyl- and 6-ethyl-6-acetyl-1,4-dithiacycloheptanes respectively:[36]

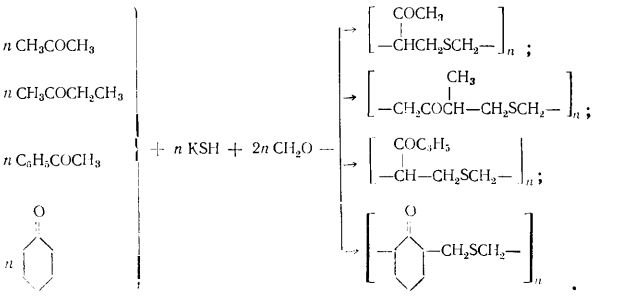


6-Benzoyl-1,4-dithiacycloheptane and 3-methyl-6,9-dithiacycloundec-2-en-1-one are obtained from acetophenone and acetone respectively under analogous conditions:[36]

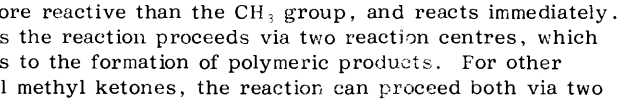


The thioalkylation reaction where hydrogen sulphide is used instead of a thiol can be compared with the Mannich reaction in which ammonia is used instead of an amine. The thioalkylation of ketones by potassium hydrogen sulphide and formaldehyde[37] is close to the thioalkylation of ketones by ethane-1,2-dithiol and formaldehyde as regards the character of the products obtained.[36]

The condensation of acetone, butanone, cyclohexanone, or acetophenone with potassium hydrogen sulphide and formaldehyde in molar proportions of 1 : 2 : 2.2 at room temperature affords polymeric ketosulphides in almost quantitative yields:

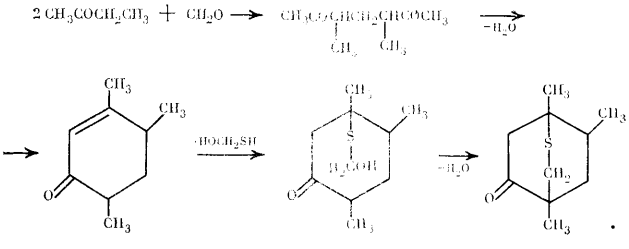


The interaction of butanone, 2-pentanone, or 2-hexanone with potassium hydrogen sulphide and formaldehyde in molar proportions of 2 : 0.5 : 1.23 at room temperature produces respectively 3,7-dimethyl-, 3,7-diethyl-, and 3,7-dipropyl-5-thianonane-2,8-diones in 15–49% yields:



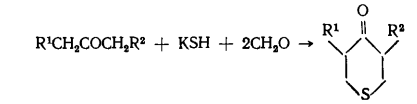
Only polymrtic products are obtained from acetone under these conditions, which can be explained by the fact that, after the substitution of one proton, the methylene group appears in the acetone molecule next to the carbonyl group, is more reactive than the CH_3 group, and reacts immediately. Thus the reaction proceeds via two reaction centres, which leads to the formation of polymeric products. For other alkyl methyl ketones, the reaction can proceed both via two reaction centres and one reaction centre (in the latter case via the most reactive methylene group with formation of 3,7-dialkyl-5-thianonane-2,8-diones).

Together with polymeric products, 1,4,5-trimethyl-7-thiabicyclo[2.2.2]octan-2-one is obtained in 20% yield on condensation of butanone with potassium hydrogen sulphide and formaldehyde in molar proportions of 1 : 0.15 : 0.36 at 50 °C:



The condensation of potassium hydrogen sulphide and formaldehyde with ketones containing two methylene groups with identical reactivities next to the carbonyl group can yield cyclic γ-ketosulphides. Thus a series of 2,6-dialkyl-4-thiacyclohexanones have been obtained in the form of mixtures of *cis*- and *trans*-isomers, with the former predominating slightly, in the course of one month at room temperature or 20–30 h at 50 °C using ketone : potassium

hydrogen sulphide : formaldehyde molar ratios of 1 : 1 : 2 in alcohol:[33]



$R^1=R^2=C_2H_5$; C_3H_7; C_4H_9; C_7H_{15}; $R^1=C_6H_5$, $R^2=CH_3$.

The yields of the cyclic γ-ketosulphides are 23–72.5%.

Amino-derivatives of ketosulphides have been obtained by the condensation of ketones with formaldehyde and aminothiols in the presence of sodium hydroxide.[33] A series of mono(dialkylaminoethylthiomethyl)-substituted ketones have been obtained from equimolar amounts of *N*-(2-mercaptoethyl)-amines, formaldehyde, and sodium hydroxide with a fivefold excess of the ketone:

$$RCOCH_2R^1 + HSCH_2CH_2NR_2^2 + CH_2O \rightarrow RCOCH(R^1)CH_2SCH_2CH_2NR_2^2 ;$$

$RR^1=(CH_2)_4$; $R_2^2=(CH_2)_5$; $R=C_6H_5$; $R^1=CH_3$; $R_2^2=(C_2H_5)_2$; $(CH_2)_5$; $(CH_2)_2O(CH_2)_2$.

The reaction of acetophenone with twice the molar amounts of *N*-(2-mercaptoethyl)amine, formaldehyde, and sodium hydroxide gave rise to a series of bis(dialkylaminoethylthiomethyl)-substituted ketones:

$$C_6H_5COCH_3 + 2HSCH_2CH_2NR_2 + 2CH_2O \rightarrow C_6H_5COCH(CH_2SCH_2CH_2NR_2)_2 ;$$

$R_2=(C_2H_5)_2$; $(CH_2)_5$; $(CH_2)_2O(CH_2)_2$.

Tetrakis(dialkylaminoethylthiomethyl)-substituted ketones have been synthesised from acetone with four molar amounts of *N*-(2-mercaptoethyl)amine, formaldehyde, and sodium hydroxide:

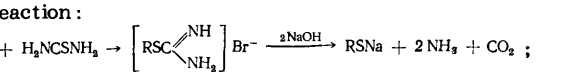
$$CH_3COCH_3 + 4HSCH_2CH_2NR_2 + 4CH_2O \rightarrow$$
$$\rightarrow (R_2NCH_2CH_2SCH_2)_2CHCOCH(CH_2SCH_2CH_2NR_2)_2 ;$$
$$R_2=(C_2H_5)_2, (CH_2)_5 .$$

3-Ethylthiomethyl-2-butanone has been obtained[38] in 80% yield by thioalkylating butanone with ethanethiol using the method which we have described:

$$CH_3COCH_2CH_3 + C_2H_5SH + CH_2O \rightarrow CH_3COCH(CH_3)CH_2SC_2H_5 + H_2O .$$

The vacuum distillation of the reaction products led to the isolation of high-molecular-weight fractions of the hydroxymethyl derivative of 3-ethylthiomethyl-2-butanone in 80% yield, but the position of the hydroxymethyl group in this compound was not established.

In the thioalkylation of ketones, Babakhanova et al.[39] used as a thiol component alkaline solution of *S*-alkylisothiuronium salts, which were obtained by the reaction of alkyl bromides with thiourea. They established that the side products resulting from the alkaline decomposition of *S*-alkylisothiuronium salts do not affect the yield of the ketosulphides, which amount to 80–90% relative to the alkyl bromides used in the reaction:



$$RSNa + CH_3COCH_2CH_3 + CH_2O \rightarrow CH_3COCH(CH_3)CH_2SR ;$$
$$R=C_2H_5, C_3H_7, C_4H_9 .$$

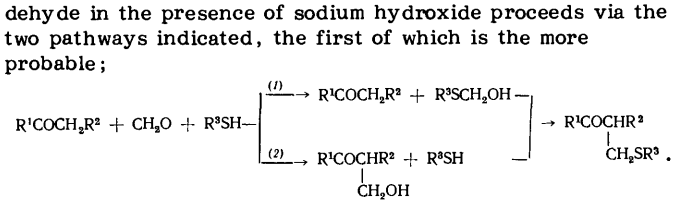
Ketosulphides have been obtained by the condensation of ketones, 1,3-diketones, or β-ketoacids esters with thiols and aldehydes in THF at 70 °C in the course of 5 h in the presence of catalytic amounts of concentrated sulphuric acid:[40]

$$RCOCH_2R^1 + R^2CHO + R^3SH \xrightarrow{H^+} RCOCH(R^1)CH(R^2)SR^3 + H_2O ;$$

$R=CH_3$; $R^1=CH_3CO$; $R^2=R^3=C_2H_5$; $RR^1=(CH_2)_4$; $R^2=H$; $R^3=C_2H_5$; C_6H_5; $RR^1=(CH_2)_5$; $(CH_2)_3$; $R^2=H$; $R^3=C_3H_5$; $R=CH_3$, $R^1=CH_3CO$; C_3H_5CO; $COOC_2H_5$; $R^2=H$; $R^3=C_3H_5$; $R=C_6H_5$; $R^1=COOC_2H_5$; $R^2=H$; $R^3=C_6H_5$.

The yields of the ketosulphides amount to 31–92%.

It has been established experimentally[33] that the reaction involving the thioalkylation of ketones by thiols and formaldehyde in the presence of sodium hydroxide proceeds via the two pathways indicated, the first of which is the more probable;



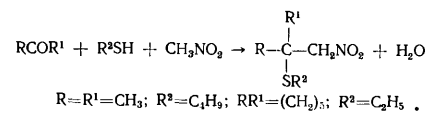
The condensation of ketones with thiols and aldehydes in the presence of strong acids[40] apparently proceeds via the formation of a carbonium-sulphonium ion as an intermediate. Thus the mechanism of this reaction is analogous to that of the Mannich reaction.[6]

4. Thioalkylation of Nitroalkanes

When a mixture of propanol, toluene-α-thiol, and nitromethane was heated at 100 °C for 30 min in the presence of catalytic amounts of piperidine, 2-(benzylthio)nitrobutane was obtained in 76% yield; 2-(benzylthio)-2-phenylnitroethane has been obtained analogously from benzaldehyde (4 h, 100 °C, yield 53%; 20 days, approximately 20 °C, yield 64%):[41]

$$RCHO + R'SH + CH_3NO_2 \rightarrow RCH(SR')CH_2NO_2 + H_2O ;$$
$$R=C_2H_5, C_6H_5, R'=C_6H_5CH_2 .$$

Ketones have also been used in this reaction instead of aldehydes, but they proved to be less reactive. On refluxing in the presence of piperidine (for 24 h), 1-(ethylthio)-1-nitromethylcyclohexane has been obtained in 50% yield from cyclohexanone, ethanethiol, and nitromethane, while 2-(butylthio)-2-methylnitropropane has been synthesised in 58% yield from acetone, butanethiol, and nitromethane:

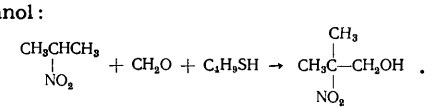


$R=R^1=CH_3$; $R^2=C_4H_9$; $RR^1=(CH_2)_5$; $R^2=C_2H_5$.

It has been suggested[41] that the condensation of nitroalkanes with aldehydes or ketones proceeds via the intermediate formation of nitro-olefins to which thiols then add:

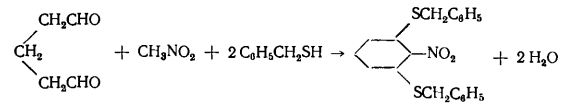
$$RCHO + CH_3NO_2 \rightarrow RCH(OH)CH_2NO_2 \xrightarrow{-H_2O} RCH=CHNO_2 \rightarrow$$
$$\xrightarrow{R'SH} RCH(SR')CH_2NO_2 .$$

The interaction of 2-nitropropane, formaldehyde, and butanethiol in the presence of piperidine yields 2-methyl-2-nitropropanol:

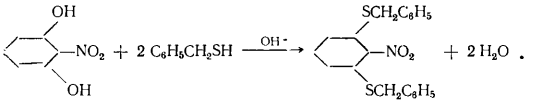


The latter is not dehydrated with formation of a nitro-olefin and the thioalkylation reaction does not take place. The behaviour of other nitroalkanes in this reaction has not so far been investigated.

1,3-Bis(benzylthio)-2-nitrocyclohexane has been obtained from glutaraldehyde, nitromethane, and toluene-α-thiol in the presence of sodium hydroxide:[42]



The same product is obtained under analogous conditions from toluene-α-thiol and 2-nitrocyclohexane-1,3-diol:



The latter is apparently an intermediate in the reaction described above.

Thus the condensation of nitromethane with thiols and aldehydes (or ketones) results in the substitution of the mobile proton of nitromethane by the thioalkyl group and the reaction can be formally classified as a thioalkylation reaction although the mechanism is different from that of other such reactions.

5. Thioalkylation of 1,3-Disulphones

The thioalkylation of sulphones was first investigated by the authors of the present review.[43] Benzyl phenyl sulphone, bis(phenylsulphonyl)methane, and bis(butylsulphonyl)-methane were used as the sulphones, whilst the thiols were butanethiol, 2-methylpropane-2-thiol, cyclohexanethiol, and benzenethiol. It was established that the above sulphones and thiols can be arranged in the following sequences in terms of their reactivity in the thioalkylation reaction:

$$(C_6H_5SO_2)_2CH_2 > (C_4H_9SO_2)_2CH_2 > C_6H_5SO_2CH_2C_6H_5 ;$$
$$t\text{-}C_4H_9SH > \text{cyclo-}C_6H_{11}SH > C_4H_9SH > C_6H_5SH .$$

The sulphone thioalkylation products have been obtained in 9–93% yields from equimolar amounts of the sulphone, the thiol, a 34% aqueous solution of formaldehyde, and sodium hydroxide in alcoholic solution with heating (to 50–55 °C; 78 °C in the case of benzyl phenyl sulphone) until the qualitative test for the thiol was negative (c.f. Houben-Weyl[44]):

$$RSO_2CH_2R^1 + R^2SH + CH_2O \rightarrow RSO_2CH(R^1)CH_2SR^2 + H_2O ;$$
$$R = C_6H_5;\ R^1 = SO_2C_6H_5;\ R^2 = C_4H_9;\ \text{cyclohexyl};\ C_6H_5;$$
$$R = C_4H_9;\ R^1 = SO_2C_4H_9;\ R^2 = C_4H_9;\ \text{cyclohexyl};$$
$$R = R^1 = C_6H_5;\ R^2 = C_4H_9;\quad t\text{-}C_4H_9;\ \text{cyclohexyl} .$$

The thioalkylation of 1,3-disulphones with formaldehyde and potassium hydrogen sulphide has also been investigated.[45] The reaction was carried out in a mixture of dioxan and methanol at room temperature using the molar ratios 1 : 3-disulphone : KSH : CH_2O = 2 : 1 : 2. 1,1,5-5-Tetrakis-(butanesulphonyl)-3-thiapentane, 1,1,5,5-tetrakis(cyclo-hexanesulphonyl)-3-thiapentane, 1,1,5,5,-tetrakis(benzene-sulphonyl)-3-thiapentane, and 1,2,6,7-tetrakis(benzene-sulphonyl)-4-thiaheptane have been obtained from bis(butanesulphonyl)methane, bis(cyclohexanesulphonyl)-methane, bis(benzenesulphonyl)methane, and 1,2-bis-(benzenesulphonyl)ethane respectively:

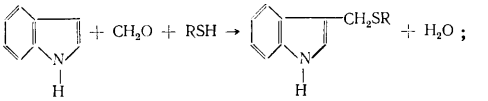
$$2(RSO_2)_2CH_2 + 2CH_2O + KSH \rightarrow (RSO_2)_2CHCH_2SCH_2CH(SO_2R)_2 ;$$
$$R = C_4H_9;\ \text{cyclohexyl};\ C_6H_5 ;$$
$$2C_6H_5SO_2CH_2CH_2SO_2C_6H_5 + 2CH_2O + KSH \rightarrow$$
$$\rightarrow C_6H_5CH_2\underset{\displaystyle SO_2C_6H_5}{\underset{|}{C}}HCH_2SCH_2\underset{\displaystyle SO_2C_6H_5}{\underset{|}{C}}HCH_2SO_2C_6H_5 .$$

The yields of the reaction products are 30–50%.

6. Thioalkylation of Other Compounds

It has been established[46] that the thioalkylation of indole, antipyrine, and 2-naphthol proceeds satisfactorily under conditions very similar to those necessary for the optimum yields of Mannich bases. The weak bases, namely indole and antipyrine, are thioalkylated in weakly acid media, while the weakly acidic 2-naphthol is thioalkylated only in a basic medium.

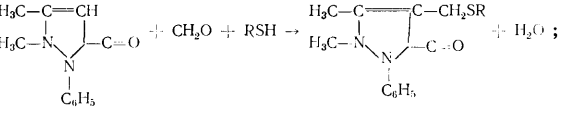
Thus the condensation of indole, a 40% aqueous solution of formaldehyde, and alkanethiols (or toluene-α-thiol) in aqueous acetic acid in the course of six days at room temperature gives rise to the corresponding 3-(alkylthiomethyl)indoles:



R = C_2H_5; C_3H_7; C_4H_9; $C_6H_5CH_2$.

The yields of the products of the reactions of alkane thiols are approximately 25%, while the reaction of toluene-α-thiol gives rise to 14% of the product; under these conditions, benzenethiol does not react.

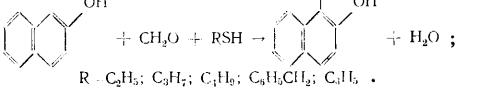
The thiolalkylation of antipyrine with paraformaldehyde and thiols in aqueous acetic acid takes place at 100 °C in the course of 23–47 h, the corresponding 4-(alkylthiomethyl)-antipyrines being obtained:



R = C_2H_5; C_3H_7; C_4H_9; $C_6H_5CH_2$; C_6H_5 .

In the reactions involving benzenethiol and toluene-α-thiol the yields of products are approximately 80%, while in the reactions of propane- and butane-thiols they are 42 and 62% respectively. Owing to its low boiling point, ethanethiol does not react satisfactorily under these conditions. 4-(Ethyl-thiomethyl)antipyrine has been obtained in 17% yield on condensing ethanediol, a 40% aqueous solution of formalde-hyde, and antipyrine in aqueous acetic acid at room tempera-ture for 14 days.

The corresponding 1-alkylthiomethyl-2-naphthols have been obtained from 2-naphthol, a 40% aqueous solution of formaldehyde, and thiols in alcohol in the presence of tri-ethylamine (6 days at room temperature):



R = C_2H_5; C_3H_7; C_4H_9; $C_6H_5CH_2$; C_6H_5 .

The yields of the condensation products are 76–79%. On decrease of the reaction time to three days, the yields are halved.

It is believed[46] that the first stage of the reaction which they investigated involves the addition of the thiols to formaldehyde with formation of alkylthiomethanols, which then react with indole, antipyrine, or 2-naphthol. This has been demonstrated by the fact that the reactions of phenyl-thiomethanol with antipyrine give rise to 4-(phenylthio-methyl)antipyrine, while the reaction of ethylthiomethanol and 2-naphthol gives rise to 1-ethylthiomethyl-2-naphthol in approximately the same yield as in the reactions of anti-pyrine or 2-naphthol with a thiol and formaldehyde. The authors do not rule out the possibility of an alternative mechanism involving the addition of indole, antipyrine, or 2-naphthol to formaldehyde with subsequent interaction of the resulting hydroxymethyl derivatives with the thiols, but they do not state that this mechanism has been confirmed experimentally.

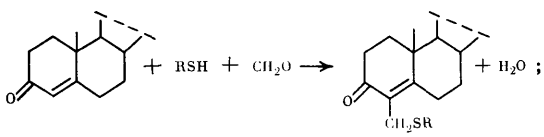
Certain compounds containing in the molecule a double bond conjugated with the carbon group, namely CO–CH=X (X = C or N), undergo the thioalkylation reaction. Thus it has been established[47] that treatment of α-ketoaldehyde ω-monoarylhydrazones with thiols and formaldehyde in acetic acid in an atmosphere of nitrogen results in the substitution of the proton in the α-position relative to the carbonyl group:

$$RCOCH{=}N{-}NHAr + R'SH + CH_2O \rightarrow \underset{\displaystyle CH_2SR'}{RCOC{=}N{-}NHAr} + H_2O;$$

R=R′=C_6H_5; Ar=C_6H_5; *p*-ClC_6H_4; *m*-ClC_6H_4; *m*-$O_2NC_6H_4$; R=CH_3; R′=CH_2CO_2H; Ar=C_6H_5.

The yields of the reaction products are 20–50%. It is believed[47] that the reaction proceeds via the intermediate formation of hemimercaptals.

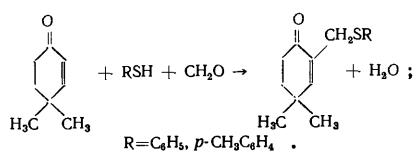
When a mixture of a 3-oxo-Δ^4-steroid, a thiol, aqueous formaldehyde (40%), triethylamine, and alcohol in proportions of 5 : 4 : 3 : 3 : 10–30 by weight (depending on the solubility of the steroid) is heated (60 °C, 30–50 h), 4-alkylthiomethyl-3-oxo-Δ^4-steroids are obtained in a satisfactory yield:[48,49]



R=C_2H_5; C_4H_9; C_6H_{11}; $C_6H_5CH_2$; C_6H_5, *p*-$CH_3C_6H_4$, furfuryl, CH_2CH_2OH; $(CH_2)_2CO_2CH_3$.

When triethanolamine is used as the catalyst and solvent and the mixture is heated to 110–150 °C, the reaction time is reduced to 8–16 h. Paraformaldehyde can be used in this reaction instead of aqueous formaldehyde and triethylamine can be replaced by other tertiary amines: trimethylamine, tri(n-propyl)amine, and *N*-methylpiperidine.

The corresponding 2-(alkylthiomethyl)substituted products are obtained in 70–72% yields by an analogous method on heating in alcohol a mixture of 4,4-dimethylcyclohex-2-en-1-one, a thiol, a 37% aqueous formaldehyde solution, and triethylamine in molar proportions of 1 : 1.5 : 1.6 : 1.4:[50]



R=C_6H_5, *p*-$CH_3C_6H_4$.

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It follows from the foregoing that the thioalkylation reactions have been little investigated. The thioalkylation of amines, hydrogen chloride, and ketones has been most thoroughly investigated hitherto, but only isolated studies have been made of the thioalkylation of other compounds.

With the exception of the thioalkylation of amines, the mechanisms of other reactions have also been little studied. All the reactions described in this review, apart from the thioalkylation of nitroalkanes, apparently proceed via a similar mechanism. The thioalkylation of nitroalkanes takes place via the intermediate formation of nitroalkenes with subsequent addition of thiols to the latter. The thioalkylation of primary and secondary amines proceeds via the mechanism of the Mannich reaction:[6] via the intermediate formation of aminomethanols $>N{-}CH_2OH$ in alkaline media or carbonium-immonium ions $>N{-}CH_2^+ \leftrightarrow >\overset{+}{N}{=}CH_2$ in acid media.

The mechanism of the thioalkylation of *NN*-dialkylanilines, ketones, indole, antipyrine, 2-naphthol, α-ketoaldehyde ω-monoarylhydrazones, and hydrogen halides is apparently analogous to the mechanism of the Mannich reaction (it involves the intermediate formation of the thiomethanols $RSCH_2OH$ in alkaline media and the carbonium-sulphonium ions $RSCH_2^+ \leftrightarrow R\overset{+}{S}{=}CH_2$ in acid media). However, one should not assume that all the compounds undergoing the Mannich reaction undergo thioalkylation or conversely. These reactions have their own specific features. For example, phenol readily undergoes the Mannich reaction but does not undergo the thioalkylation reaction. Conversely, bis(benzenesulphonyl)methane readily undergoes thioalkylation but does not produce Mannich bases.[51]

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The Solid-phase Polymerisation of Monomers with Conjugated Acetylenic Groups

V.M.Misin and M.I.Cherkashin

Published data on the solid-phase topochemical polymerisation of linear and cyclic monomers containing conjugated acetylenic groups are surveyed and the boundary conditions in this process are discussed. The structure of the monomers, is the intramolecular and supermolecular structures of the polymers, and the specific features of their chemical, physicochemical, physicomechanical, and optical properties are examined.
The bibliography includes 300 references.

CONTENTS

I. Introduction 562
II. The solid-phase polymerisation of linear symmetrical diacetylenic monomers 562
III. Special cases of the solid-phase polymerisation of monomers with $-(C\equiv C)_n$-groups 573
IV. Soluble diacetylene polymers and their properties 578
V. Monomolecular and polymolecular layers based on diacetylenes 582
VI. Mechanical properties of polydiacetylenes 584
VII. Chemical properties of polydiacetylenes 585
VIII. Polymerisation of linear compounds with separated $-C\equiv C-C\equiv C$-groups 587

I. INTRODUCTION

Fundamental synthetic studies on the solid-phase polymerisation of diacetylenic monomers containing the $-(C\equiv C)_2-$ (DA) groups were published a fairly long time ago.[1-5] At the present time such investigations have undergone a considerable development in connection with the discovery of a series of unique properties in the polymeric single crystals obtained by this procedure: thermochromism, high mechanical strength, non-linear optical properties, and a considerable anisotropy of the mechanical, optical, electrophysical, etc. properties. The available reviews on this subject, including those which were published during the preparation of this report, are devoted mainly to problems of the kinetics and mechanism of the polymerisation of DA and the magnetic, spectroscopic, and electrophysical properties of polydiacetylenes (PDA).[6-9]

In the present review attention has been concentrated on the characteristics of the structure, crystal chemistry, and morphology of the initial crystalline monomers having the general formula $R-(C\equiv C)_n-R$ ($n = 2-4$) and the corresponding polymers, the characteristic features of the mechanical and chemical properties of the polymeric crystals, and the specific features of the synthesis of soluble polydiacetylenes and DA copolymers. In addition, the reactions of various compounds containing separated $-(C\equiv C)_2-$ groups are considered. In writing this review, the authors endeavoured to cover fairly fully the available literature, reflecting at the same time the chronology of the varying and sometimes contradictory points of view on certain aspects of the solid-phase topochemical polymerisation (TPM) of acetylenes and the properties of the resulting products.

It must be emphasised that by the term topochemical polymerisation we understand a process which consists in a direct transition from the molecules of the crystalline monomer to crystallised polymer chains with retention of the crystallographic centre of gravity and symmetry of the monomeric units. The crystal lattice of the monomer is not disrupted in this process and non-crystalline intermediates are not produced. In the course of the polymerisation of such monomers, a solid solution of polymer chains in the monomer matrix is formed, i.e. the polymerisation is homogeneous.[10-12]

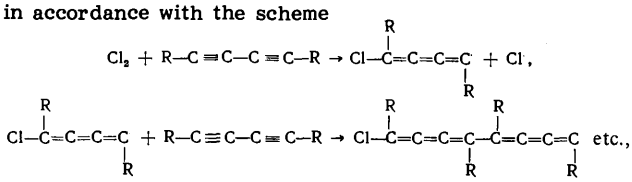
Instances of the breakdown of the crystal lattice with a corresponding change in the monomer polymerisation process are observed in real DA–PDA systems and special attention will be devoted to this aspect.

II. THE SOLID-PHASE POLYMERISATION OF LINEAR SYMMETRICAL DIACETYLENIC MONOMERS

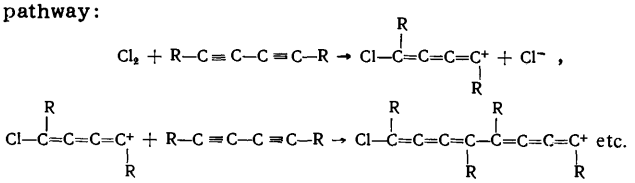
1. General Information

The acquisition of green, red, blue, or other colours by certain solid derivatives of diacetylene, for example, diols and mono- and di-carboxylic acids with a metallic lustre, which has been observed in early investigations[13-15] on illumination or heating, was subsequently interpreted as the topochemical polymerisation of these compounds.[14-16] A study of the infrared spectra of the polymers of deca-4,6-diyne-1,10-diol and its bisnaphthylurethane, the study of the electronic absorption and fluorescence spectra of the hexa-2,4-diyne-1,6-dicarboxylic acid polymer, and the detection of phthalic acid in the products of the decarboxylation and oxidation of this polymer by chromic acid (the material balance of the reaction products has not been published)[17,18] suggested[16-18] that parallel diyne molecules are converted into a polyacene macromolecule. The impossibility of the polymerisation of diynes in solution and in the melt has been explained by the absence of this type of seed outside the crystal.[14,16] Without taking into account the character of the substituents in the DA, this view was in fact reflected in the early reviews.[19-21] Subsequently the above concept was revised. Wegner[1-5] showed that the solid-phase polymerisation of DA (photochemical, radiation-induced, and mechanically initiated or thermopolymerisation at a temperature below the melting point), which proceeds in accordance with the laws of a topochemical reaction, leads to the formation of conjugated linear but not acene polymers. The polymerisation then proceeds only in those DA where the substituents contain groups capable of forming hydrogen bonds or of dipole–dipole interaction.[1,2] The attempts to polymerise such monomers in the liquid phase frequently fail. It has been shown[22] that the polymerisation of DA can be initiated by chemical initiators—gases capable

of forming radicals on the surface or in the bulk of the crystals (Cl_2, Br_2, O_3, NO_2, NOCl, PF_3, or I_2), for example, in accordance with the scheme



although the authors do not rule out an alternative reaction pathway:



Numerous symmetrical conjugated DA of different classes, examples of which are presented in Table 1, have been investigated as the monomers. However, the vast majority of the kinetic studies as well as the investigations of the structures and physicochemical and electrophysical properties of PDA have been carried out on the basis of a fairly limited range of symmetrically substituted monomers with R = CH_2OH (HD), $CH_2OC(O)NHC_6H_5$ (HDDU), $CH_2OSO_2C_6H_4.CH_3$-*p* (TS), CH_3-*N*-carbazolyl (DCHD), and $(CH_2)_nOC(O)NHCH_2C(O)O(CH_2)_mCH_3$, where $m = 1$ and $n = 3$ (3ECMU), $m = 3$ and $n = 3$ (3BCMU), $m = 1$ and $n = 4$ (4ECMU), and $m = 3$ and $n = 4$ (4BCMU), as well as a cyclic DA:

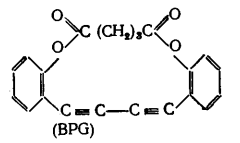

(BPG)

Table 1. Symmetrical DA (R–C≡C–C≡C–R) investigated in solid-phase polymerisation.

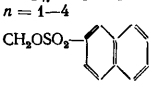
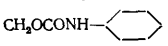
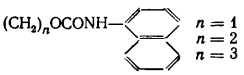
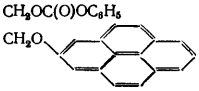
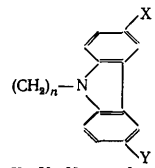
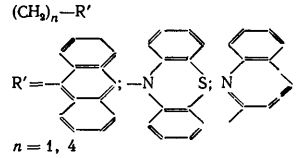
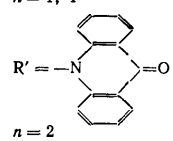
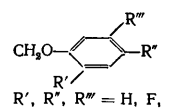
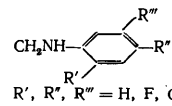
R	Refs.
CH_3	[23, 24]
$C(CH_3)_2H$	[25]
$(CH_2)_nCH_3$ n=11, 12	[26]
$CH_2C_6H_5$	[1, 2, 4]
C_6H_4R' R′=H	[5, 24, 25, 27]
R′ = *o*-, *m*-, *p*-NO_2, NH_2, $NHCOCH_3$, $NHCOC_6H_5$, $NHCONHC_6H_5$	[5]
R′-*m*-$NHCOCH_3$	[5, 28]
$(CH_2)_nOH$ n=1	[1, 2, 4, 27, 29, 30]
n=2	[23, 31, 32]
n=6—9	[33]
$CH(CH_3)OH$	[23]
$(CH_2)_nOSO_2C_6H_4R'$; n=1; R′=*n*-CH_3	[4, 23, 34, 29, 35—41]
n=2; R′=*p*-CH_3	[42]
n=4; R′=*p*-CH_3	[43]
n=1; R′=*p*-OCH_3, H	[2, 4, 44, 45]
n=1; R′=*p*-F	[46—48]
n=1; R′=*p*-Cl, *p*-Br	[46]
n=1; R′=*m*-CF_3	[47, 48]
$(CH_2)_nOSO_2C_6H_4—N=N—C_6H_5$ n = 1—4	[49, 50]
	[51]
$(CH_2)_nOCONHC_6H_5$ n = 1	[1—3, 23, 31, 34, 52, 53]
n = 2	[23]
n = 3	[23, 54, 55]
n = 4	[25, 55—58]
$CH_2OCONHC_6H_4R'$; R′=*p*-CH_3	[1, 34, 44]
R′ = *m*-Cl, *p*-Cl	[1]
	[1]
 n = 1, 2, 3	[1, 2, 4, 34] [23] [59]
$(CH_2)_2OCONHCH_3$	[23]
$(CH_2)_nOCONHC_2H_5$ n = 1	[23, 44]
n = 2, 3	[23, 55]
n = 4	[25, 60, 61]
$CH_2OCONHC_3H_7$	[44]
$(CH_2)_4OCONHCH(CH_3)_2$	[62]
$CH_2OCONH(CH_2)_nCH_3$ n = 3	[1, 2, 4]
n = 5, 7, 11	[23]
$(CH_2)_nOCONHC_6H_4—N=N—C_6H_5$ n = 1—4	[49, 50]
$CH(CH_3)OCONHC_6H_5$	[2]
$C(CH_3)_2OCONHC_4H_9$	[2]
$CH_2OCO(CH_2)_nCH_3$ n=17	[3]
n=4, 6, 8, 10, 12, 14, 16	[63]
$CH_2OCOC_6H_4R'$ R′=H	[1, 4, 23]
R′=*o*-COOH	[1, 2]
$CH_2OC(O)OC_6H_5$	[1, 2, 4]
	[64]

Table 1 (contd.).

R	Refs.
$(CH_2)_nOCONHCH_2COO(CH_2)_mCH_3$ m = 1, 3; n = 1—4	[65, 66]
$(CH_2)_nCOOM$ n = 1—4; M = H, Li, Na, K	[67, 68]
$(CH_2)_nOCONHCH_2COOM$ n = 3, 4; M = H, Li, Na, K	[67, 68]
$(CH_2)_nCOOR'$ n=6—9	
R′=CH_3, C_2H_5, $CH_2C_6H_5$	[33]
$(CH_2)_nR'$ n=6—9	
R′=Hal, CN	[33]
	
X=Y=H; n = 0	[25, 69]
n = 1	[1, 25, 69—73]
n = 3	[74]
n = 4	[69]
X, Y=Cl, Br, NO; n=0 — 10	[75]
$(CH_2)_n—R'$	
	
n = 1, 4	[69]
	
n = 2	[69]
	
R′, R″, R‴ = H, F, NO_2, CF_3	[76, 77]
	
R′, R″, R‴ = H, F, CH_3, CF_3, NO_2	[78]
$(CH_2)_nN(CH_2)$—	
n = 1, 4	[69]

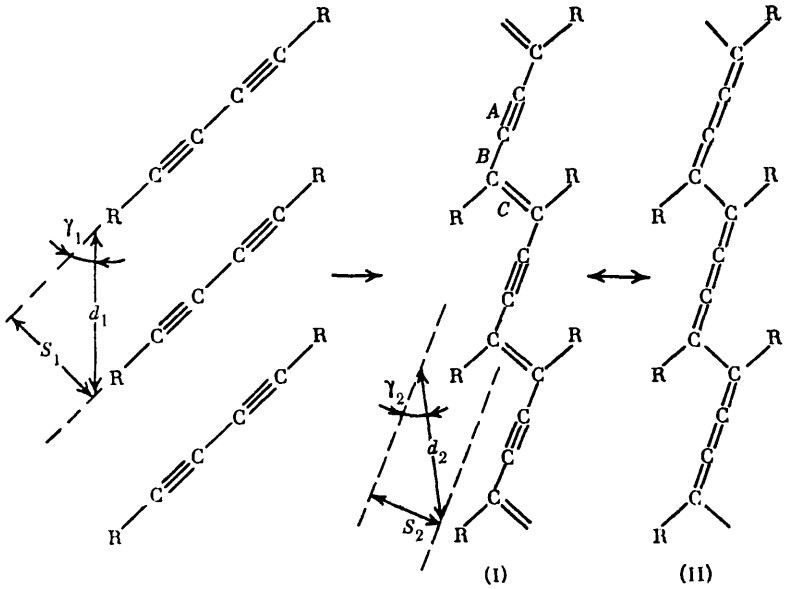


Figure 1. Schematic illustration of the solid-phase polymerisation of monomers with the $-C\equiv C-C\equiv C-$ groups: (I) and (II) are respectively the enyne and butatriene mesomeric forms of the polymer chains; the parameters d, S, and γ describe the topology of the monomer molecules and the polymer chain; B, C, and A are the length of single, double, and triple bonds.[9]

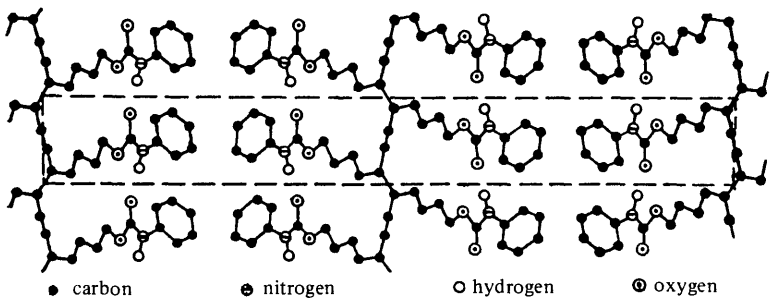


Figure 2. Schematic illustration of the packing of DA [R = $(CH_2)_4OCONHC_6H_5$] in the crystallographic cell. Projection on to the *bc* plane.[81]

Various specially synthesised deuterio-derivatives of TS have been used in the study of the isotope effects in the polymerisation of this DA.[79,80]

2. The Essential Conditions in the Polymerisation of Diacetylenes

The requirements which must be met by the DA polymerising via the TPM mechanism have been discussed in a review.[9] In the present communication the factual data on which these requirements are based have been extended. The changes occurring in the monomer–polymer transition, in conformity with the principles of a topochemical polymerisation of DA, are illustrated in Fig.1. The polymerisation reaction involves the 1,4-*trans*-addition and proceeds via specific rotations of the monomer units about the centres of gravity and via shifts of the centres of gravity. It is determined by the characteristic features of the packing of the monomer in the crystal lattice and proceeds without the evolution of side products and with formation of polymer chains extended parallel to the crystallographic *b* direction (Fig.2).[81]

The absence of the polymerisation of DA molecules in solution and in the melt has in fact been explained by the disordered nature of its molecules.[1,37] However, the presence of polar or interacting (Fig.2) side groups is not a sufficient condition for the occurrence of solid-phase polymerisation, since certain types of substituent hinder it. Indeed, diphenylbutadiyne (DPB) does not polymerise in the

solid phase, since large shifts and rotations of the molecules are required for this purpose.[5,27,28,81] All the symmetrical diamino-derivatives of DPB are also inactive. Nitro-, phenylureido-, acetamido-, or benzamido-groups in the 4- and 4'-positions in DPB hinder the topochemical polymerisation, while those in the 2- and 2'-positions and particularly 3- and 3'-positions of the corresponding DA promote it.[5]

In a series of DA with the substituents R = $CH_2OC(O).(CH_2)_nCH_3$ (n = 4, 6, 8, 10, 12, 14, 16), the rate of polymerisation increases with increasing length of the paraffinic side group, reaching a maximum for n = 8 and then falling owing to the characteristics of the packing of the paraffinic side chains in each member of the series considered.[63]

The presence of α-substituents at the $-(C\equiv C)_2-$ group gives rise to steric hindrance in topochemical polymerisation. Diyne monomers with the substituents R = $CH(CH_3)OC(O).NHC_6H_5$ or $C(CH_3)_2OC(O)NHC_4H_9$ do not therefore polymerise, in contrast to the extremely reactive monomers with the substituents R = $CH_2OC(O)NHC_6H_5$ or $CH_2OC(O)NHC_4H_9$.[1,2,4,23,25]

In view of the need to create a suitable crystal structure in the solid monomer, the polymorphism of the DA assumes a special importance. Thus HDDU, recrystallised from various solvents or their mixtures, has several different crystalline modifications among which only one exhibits a high reactivity.[1,10,82,83] This is caused by the fact that only the monomer recrystallised from a dioxan–water mixture has the necessary packing as a result of the presence of dioxan molecules in the centre of the unit cell forming hydrogen-bonded chains with other neighbouring DA molecules.[84] When dioxan is removed by evacuating the specimens, the monomer loses its reactivity.[84]

Polymerised DA with R = $CH_2OCONHC_6H_4CH_3$-m can be obtained in the form of "orange" and "blue" modifications, whose colour is associated with a small admixture of PDA. After being kept in dioxan vapour, the "orange" modification undergoes a "solvatochromic" solid-phase transition to the more reactive "blue" phase, which is accompanied by an increase of the size of the crystals in one of the directions by ~25%. This is associated with the insertion of dioxan in the single crystal, the formation of hydrogen bonds, and the assumption of a planar conformation by the PDA formed. Extraction of the non-polymerised monomer from the "blue" modification (λ_{max} = 650 nm) leads to the appearance of a red residue (λ_{max} = 550 nm) as a result of the reverse process: the removal of strain from the crystal and the transition of the monomer to a non-planar conformation having different electronic structures.[85]

After being kept in the vapours of polar solvents, the inactive modifications of other urethane DA are also able to undergo a transition into reactive modifications. The transition is accompanied by the appearance of an intense colour associated with the formation of polymer chains in the crystal matrix of the DA and depending on both the structure of the DA and on the type of solvent.[85]

A strong influence of the substituents on the capacity for polymerisation, associated with the packing of the monomer, has been observed also in a series of symmetrical DA (III):

$$RC_6H_4SO_2OCH_2C\equiv C-C\equiv CCH_2OSO_2C_6H_4R \quad \text{(III)}$$

R = H, m-CF_3, p-CH_3, p-OCH_3, p-F, p-Cl, p-Br.

Thus the p-bromo-,[46,47] p-fluoro-,[46] and p-chloro-derivatives of compound (III)[46,47,86] are inactive in solid-phase polymerisation. X-Ray diffraction studies have shown that the lack of reactivity of the chloro-derivative is associated with the unsuitable packing of the monomer.[86] However, a crystalline modification of the p-fluoro-substituted sulphonate, less reactive than TS, has been found.[47] Reactive modifications of compound (III) with R = p-Cl or p-Br, whose melting points are ~50° lower than those of the corresponding inactive forms, have been obtained by crystallisation from a highly supersaturated ethereal solution†. The diacetylenes (III) with R = H, p-OCH_3, or m-CF_3 polymerise in the solid phase and the p-methoxy-derivatives can be obtained in both reactive and inactive forms.[46,47] According to X-ray diffraction studies,[46,47] the side groups in the inactive form rotate above the –O– bond, so that the distance between neighbouring molecules is much greater than that necessary for solid-phase polymerisation. TS (R = p-CH_3) is the most reactive.

The influence of not only the nature of the substituent in the side groups of DA but also of its isotopic composition on reactivity in TPM has been observed. Thus the infrared spectroscopic and differential scanning calorimetric (DSC) studies of the kinetics of the thermal topochemical polymerisation of a series of TS derivatives revealed a decrease of the rate of the autocatalytic stage in a series of DA with different substituents, i.e.

$$CH_2OSO_2C_6H_4CH_3\text{-}p > CH_2OSO_2C_6H_4CD_3\text{-}p > {}^{13}CH_2OSO_2C_6H_4CH_3\text{-}p > CD_2OSO_2C_6D_4CD_3\text{-}p > CD_2OSO_2C_6H_4CH_3\text{-}p,$$

while E_a remained unchanged. During the induction period, the opposite isotope effect was observed. The difference between the rates of reaction has been explained by the variation of the pre-exponential factor for the rate constant, which is attributed to the different lifetimes of the excited state responsible for the chain initiation.[79,80] A decrease of the rate of reaction has also been observed for DA with other substituents: $CH_2OCONHC_6H_5 > CD_2OCONHC_6H_5$.[79]

In order to determine the reactivities of crystallised DA, it is necessary to take into account the contribution of the strain energy of the crystal and the change in chemical energy in the monomer–polymer transition. An estimate of the free energy barrier to molecular movement, required for topochemical polymerisation, is essential in determining the contribution of the energy of the crystal. However, the exact determination of the magnitude of this barrier is very difficult. Allowance for the limitations examined above, arising in the solid-phase polymerisation of DA, led to the development of the principle of the minimum mean square atomic displacement (MMAD) necessary for polymerisation,[81,87] which makes it possible to predict the possibility of the topochemical polymerisation of both different DA and their different crystalline modifications. Parameters most suitable for the description of the topology of the reacting monomer molecules and the resulting polymer chain were selected for this purpose. Such parameters are the vector d_1 and the angle γ_1 in the monomer and the vector d_2 and the angle γ_2 in the polymer, linked by the relation $a = S/\sin\gamma$ (Fig.1). The values of d_1 and γ_1 have been determined for a large number of monomers (Table 2) and have been found to vary in the ranges d_1 = 4.1–8.5 Å and γ_1 = 41–90°. For the polymers, d_2, γ_2, and S_2 are respectively 4.9 Å, 13.4°, and 1.2 Å.

For the most reactive modifications, the monomer parameter S_1 should be ~3.4 Å (twice the van der Waals radius of the carbon atom which can obtain in monomers of the type $HC\equiv C-C\equiv CH$ and $NC-C\equiv C-C\equiv C-CN$). However, owing to the large bulk of the substituent side groups, it actually assumes larger values, reaching ~4.7 Å for the very bulky t-butyl substituents. A polyconjugated chain with the corresponding changes in the geometrical dimensions by the

†V.Enkelmann, J.Mater.Sci., 1980, 50, 951.

amounts Δd and $\Delta\gamma$ is formed in the course of the topochemical polymerisation. The mean square displacements necessary for the polymerisation reaction in solid DPB, HD, and its benzoate were determined by a formula[81]

$$\text{HCAC} = {}^1/_2\left\{\sum_{i=1}^{4}\left[\int_{\gamma_1}^{\gamma_2}(A_i + B_i\sin\theta)^{1/2}\,d\theta\right]^2\right\}^{1/2},$$

where

$$A_i = r_i^2 + {}^1/_4[(d_2-d_1)/(\gamma_2-\gamma_1)]^2;\quad B_i = r_i[(d_2-d_1)/(\gamma_2-\gamma_1)],$$

r_i is the length of the vector joining the centre of the molecule to the ith carbon atom in the linear group $C\equiv C-C\equiv C$ in the monomer, and θ varies from γ_1 to γ_2.

Although the above analysis does not include certain details, for example, the anisotropy of the intermolecular forces and the allowance for the difference between the lengths of the polymer chain and between the numbers of the initial monomer molecules (i.e. the principle holds best for low degrees of conversion), nevertheless the calculations yielded a satisfactory agreement with the experimental result: the mean square displacements increased with decrease of the polymerisation capacity of the monomers estimated in the investigations.[81]

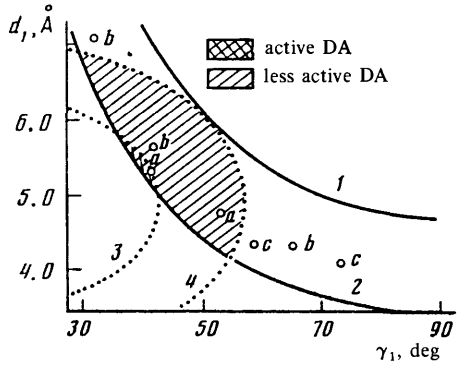


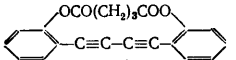
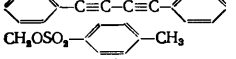
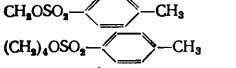
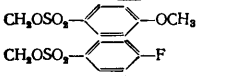
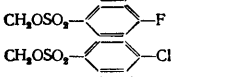
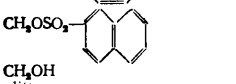
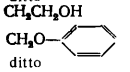
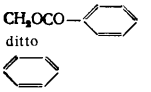
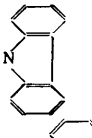
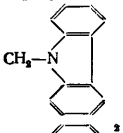
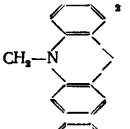
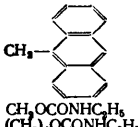
Figure 3. Determination of the ranges of the structural parameters, d_1 and γ_1 corresponding to the reactive and inactive modifications of DA: *a*) hexadiynediol; *b*) hexadiyne; *c*) hexadiyne dibenzoate; 1) S_1 = 4.7 Å; 2) S_1 = 3.4 Å; 3) MMAD = 0.72 Å; 4) MMAD = 1.08 Å.[81]

Fig.3 [81] presents as an example the structural parameters (dashed lines) for two values of MMAD: 0.72 Å (corresponds to the most reactive crystalline HD phase) and 1.08 Å (corresponds to crystalline DPB which is almost inactive in topochemical polymerisation; although the crystals become coloured, the polymer can be isolated). The crystalline modifications of monomers with coordinates lying to the right of the MMAD = 1.08 Å curve are inactive in topochemical polymerisation, which agrees with experimental observations. In addition, curves (continuous lines) representing the $d_1 = S_1/\sin\gamma_1$ relation for two values of S_1 are plotted in Fig.3. The circles in Fig.3 denote the coordinates of d_1 and γ_1 observed for the crystalline modifications of monomers with approximately the same minimum separations S_1. Thus the curves plotting in Fig.3 make it possible to determine the regions in which the parameters d_1 and γ_1 correspond to high (narrower region) and low (broader region) reactivities.

For example, in the case where S = 3.4 Å (curve *2*) the region of the parameters corresponding to a very high reactivity is bounded by the ranges $\gamma_1 \cong 36$–$42°$ and $d_1 \cong 5.0$–5.9 Å, while the region corresponding to a lower reactivity is bounded by the broader ranges of the parameters $\gamma_1 \cong 29$–$55°$ and $d_1 \cong 4.2$–6.9 Å.

Analysis of Fig.3 shows that one cannot except an appreciable topochemical polymerisation of monomers with $S_1 \geq 4.7$ Å, since the curves corresponding to the MMAD and S_1 = 4.7 Å (curve *1*) are hardly overlapped. Indeed, reactive phases of DA of the type $R-C(CH_3)_2-C\equiv C-C\equiv C-C(CH_3)_2-R$ are unknown.[2,31]

Table 2. Specific features of the packing in the single crystals of the DA $R^1-C\equiv C-C\equiv C-R^2$ and the possibility of topochemical polymerisation ($R^1 = R^2$).

R^1	Parameter from Fig.1		Reactivity in TPM	Refs.
	d_1, Å	γ_1, deg		
	4.93	46	+[4]	[88]
	5.42	90	—	[88]
	5.11	44	+	[89]
	5.19	47.9	+	[90]
	5.80	45	—	[91]
	5.18	—	+	[47]
	5.03	67	—	[86]
	5.42	62	—	[51]
CH_2OH	4.76	41	+[4]	[92]
ditto	4.09	73.4	—[5]	[92]
CH_2OH^1	4.87	49.6	+[4]	[93]
CH_3	5.65	42	+[6]	[81]
ditto	4.31	65.3	—[5]	[81]
CH_2CH_2OH	4.85	48	+[4]	[94]
	8.53	77	—	[95]
ditto	7.47	73	—	[95]
	4.35	58	+[6]	[96]
ditto	8.48	40	—	[96]
	6.04	50.9	+[6]	[27]
	4.66	90	—	[97]
	4.55	60	+[7]	[98]
	4.35	61.5	—	[99]
	4.36	61.0	—	[99]
$CH_2OCONHC_6H_5$	5.05	43	+	[100]
$(CH_2)_4OCONHC_6H_5$	5.23	42	+	[101]
$(CH_2)_8CH_3$[3]	4.76	45	+	[102]

Remarks: [1]$R^2 = CH_3$. [2]$R^2 = CH_2$(9-anthryl). [3]$R^2 = (CH_2)_8COOH$. [4]Complete conversion is not attained. [5]Topochemical polymerisation is impossible according to the MMAD principle. [6]Reactive under pressure. [7]Phase transition in the course of topochemical polymerisation.

It has been suggested that this principle for the determination and comparison of the reactivities in topochemical polymerisation with the aid of the MMAD principle can be extended also to other systems as well. It has been shown experimentally that the most reactive DA are those which have the following parameters: $d_1 \cong 5$ Å, $\gamma_1 \cong 45°$, and S_1 in the range $3.4 < S_1 < 4.0$ Å (Table 2). For example, the non-polymerising DA (III) with R = *p*-Cl has $d_1 \cong 5$ Å, which corresponds to a high reactivity of the monomer.[86] However, $\gamma_1 \cong 67.0°$ is outside the limits corresponding to a reactive modification of DA.[81] On the other hand, in one of the modifications of DA with R = $CH_2OC(O)NHC_6H_4CH_3$-*m* the vectors of the neighbouring molecules are not parallel, intersecting at an angle of 72°, which is inconsistent with the mechanism of topochemical polymerisation. However, the short distance between the neighbouring terminal carbon atoms is sufficient for the reaction to occur albeit with a low yield. The exposure of this modification to dioxan vapour leads to the formation of a highly reactive modification containing the solvent.[85]

The second factor influencing the specific features of the topochemical polymerisation of the monomers and the morphology of the resulting PDA is the inconsistency between the parameters of the crystal cells of the monomer and the polymer, which leads to strain and hence to defects in the single crystal on polymerisation of the monomer, which diminished the degree of conversion of DA and prevents the formation of a polymer having a high molecular weight.

The influence of this factor has been observed by means of X-ray diffraction for HD [27] in the course of the polymerisation of which (^{60}Co γ-radiation, dose 5–100 Mrad, dose rate 1 Mrad h^{-1}) the linear parameters and the angle γ of the unit cell varied continuously with the corresponding variation of the density of the crystal (Fig.4). The distance between the centres of the reacting monomer molecules then diminished by 0.44 Å and the axis of the conjugated C≡C–C≡C bonds was rotated by an angle of ~28°.

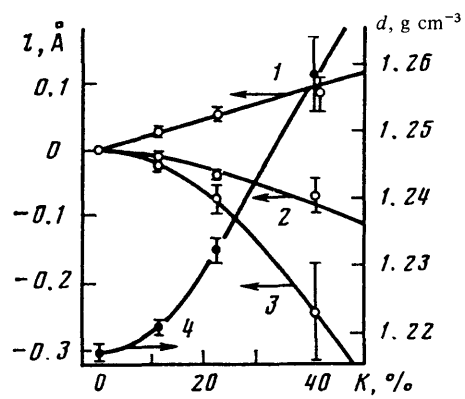


Figure 4. Variation of the parameters *l* of the unit cell [1) Δ*a*; 2) Δ*c*; 3) Δ*b*] and the density *d* (curve 4) as a function of the degree of conversion *K* of hexa-2,4-diyne-1,6-diol.[27]

The polymerisation reaction results in the formation of a solid solution of the polymer chains in the monomer matrix. However, when a specimen of this kind polymerised up to low degrees of conversion (50 Mrad) is kept for two months at room temperature, phase separation takes place, yielding separately the monomer and the amorphous phase of the polymer.[27] The conversion of PDA into the amorphous form also takes place on topochemical polymerisation of the monoclinic HD phase up to high degrees of conversion. The reason for this is the deviation of the centre of the monomer unit of the polymer chain from the centre of the corresponding monomer molecule as a result of a continuous translational movement initially over a distance $d_1 - d_2 = 0.44$ Å and then, as the polymer chain grows, over a longer distance. The enhancement of the amorphous X-ray scattering with increasing conversion in the range 0–69% corresponds experimentally to this process. A similar inhomogeneous course of the solid-phase polymerisation has been observed by Raman spectroscopy for HD biscaprilate.[45] A similar behaviour is observed on thermal polymerisation of HD.[30] Because the shifts are $d_1 - d_2 \cong 0$ for the HDDU phase containing dioxan, appreciable amorphous scattering does not occur up to quantitative conversion.[10,83]

Since the distribution of well-separated polymer chains along their lengths is irregular for long $d_1 - d_2$ distances and high degrees of conversion, the synthesis of PDA single crystals with $d_1 - d_2 \neq 0$ should probably be carried out at a suitable higher temperature where the molecular mobility essential for the longitudinal rearrangement of the system increases.

Another example of the synthesis of amorphous PDA is provided by the solid-phase polymerisation of HD bis-stearylurethane with subsequent extraction of the monomer which has not reacted and the isolation of the polymer having the character of a nematic liquid crystal.[3] The authors believe that the thermodynamically unfavourable strained or kinetically stable polymer conformation having a high free energy can exist only in the presence of a monomer lattice, ensuring thereby an "enforced" isomorphism of the polymer and monomer. The isolation of such a polymer leads to its conversion into an amorphous form with the corresponding decrease in its free energy.

However, for example, in the case of poly-TS, an increase of the degree of crystallisation of the extracted PDA with increasing degree of conversion has been noted.[36] This phenomenon is caused by the isolation of the polymer chains in the polymer matrix at lower conversions. With increase of the amount of polymer, neighbouring chains appear. Calculations based on the random formation of nuclei have demonstrated a significant increase in the number of adjoining chains and hence of the degree of crystallinity in the extracted polymer for conversions in excess of 10%, which has in fact been observed.[36]

In a general form, the criteria of phase stability have been examined[81] from the standpoint of the dependence of the overall free energy of the system on the degree of conversion. Here it is assumed that the overall free energy is made up of intramolecular and intermolecular components and should decrease with increased degree of conversion. Since the intramolecular contribution can be represented as a linearly diminishing function of the monomer–polymer transformation (both the monomer and the polymer must then exist in conformations with the minimum free energy), the change in the overall free energy of the system is influenced significantly by the character of the variation in the intermolecular contribution. Fig.5 presents an example of a free energy diagram, conforming to these general postulates, for the case where topochemical polymerisation proceeds with phase separation.[64]

The third general condition governing the possibility of topochemical polymerisation is the correspondence between the symmetries of the structural units in the monomer and

polymer crystals. In conformity with the possible types of symmetry for the monomer units in PDA and with the retention of the specificity of the solid-phase reaction, there exist specific types of symmetry of the monomer necessary for the synthesis of specific PDA chains: the monomer symmetries are of the 1, $\bar{1}$, 2, *m*, 2/*m* types for the synthesis of *trans*, *trans*-polymers and 1, 2, *m*, *mm*2 for the synthesis of *cis*, *trans*-polymers. Examination of the types of symmetry for a series of DA (HDDU and HD) and DA with R = $CH_2OC(O)C_6H_5$ and C_6H_5 has shown that their topochemical polymerisation can proceed with formation of *trans*,*trans*-PDA. Furthermore, in theory the type of symmetry of the crystalline HDDU phase should enable it to polymerise with formation of *cis*,*trans*-PDA single crystals (it has been established experimentally that this monomer polymerises with formation of only *trans*,*trans*-PDA).[84] However, in practice all the conjugated DA, including cyclic DA, are packed in crystals in such a way that the solid-phase polymerisation yields either the *trans*, *trans*-polymer or the monomer does not polymerise.[103]

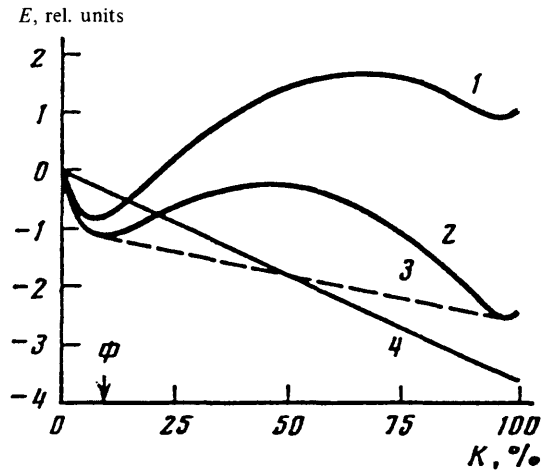


Figure 5. The free energy (E) diagram for the case where the solid-phase polymerisation cannot occur up to high degrees of conversion K owing to phase separation into isomorphous or non-isomorphous phases: 1) intermolecular contribution (one phase); 2) total free energy (one phase); 3) total free energy (two phases); 4) intramolecular contribution. The point Φ denotes the limiting conversion without phase separation.[64]

It has been observed that polymerisation with formation of a single crystal does really occur in the case of HDDU but not for TPB and HD dibenzoate,[1,5,23,27] since in the last two cases polymerisation requires excessive molecular displacements. In other words, the topochemical polymerisation of TPB and HD dibenzoate is allowed by symmetry conditions but is prohibited by the minimum displacement principle. The solid-phase polymerisation of HD is likewise not prohibited by the symmetry criterion and occurs in practice at least up to low degrees of conversion.[27] However, as reported above, owing to the displacement of the centres of the monomer units (by $d_1 - d_2$), the correspondence between the topologies of the polymer chain in the monomer units subsequently breaks down and the final polymer is amorphous. In such cases the "recrystallisation" of the reactive form in the direction of the PDA chains is necessary to increase the degree of conversion and the degree of crystallinity.

Thus the set of the specific requirements mentioned above which must be met by the topochemical polymerisation of diacetylenes may be formulated as the following criteria:[81,87] the occurrence of the minimum displacements of the atoms of the reacting molecules, phase stability of PDA in the DA matrix, and the retention of crystallographic symmetry elements in the DA → PDA transition. Only the simultaneous fulfillment of these criteria permits the actual occurrence of the topochemical polymerisation of the monomers.

The solid-phase polymerisation (γ-irradiation; 6.3 Mra; −78 °C) of thin films of butadiyne, i.e. DA having the smallest R = H substituents, has been described. However, the infrared spectra indicate the aromatic character of the monomer which implies, according to the authors,[104] the isotactic linear 1,2-addition to the C≡C bond and subsequent cyclisation.

The characteristic features of the DA polymerisation processes as well as the specificity of the structure and properties of the intermediate compounds and the final PDA have been investigated by various methods: gravimetrically with extraction of the monomer,[11,25,35–38,79,105,106] contraction of single crystals,[76,107,108] flash photolysis,[102] method employing X-ray diffraction,[27,30,35] proton spin–lattice relaxation,[110] DSC,[25,27,76,77,105,111–115] Brillouin scattering,[56,116] photoacoustic methods,[117–119] optical spectroscopy,[35,82,105,120–123] scattered reflected light spectroscopy,[35,38,46,124] EPR,[30,125–132] infrared spectroscopy,[80,133] Raman spectroscopy,[31,35,41,45,46,134,135] and molecular weight distribution.[136] When particular conditions are met, various methods for the investigation of the topochemical polymerisation kinetics (for example, the gravimetric method, DSC, and electronic spectroscopy) yield satisfactorily concordant results.[105]

3. The Crystal and Molecular Structures of Diacetylenes and Their Polymers

The solid-phase reactions of DA which satisfy the criteria for topochemical polymerisation result in the formation of crystalline linear polymers. Well formed acicular crystals up to 5 cm long have been obtained by the method described on the basis of HDDU,[53] while large crystals weighing more than 1 g have been synthesised from TS.[125,137] The possibility of obtaining larger PDA crystals (up to 15 cm long and weighing up to 10 g) has been reported.[87]

Studies by optical and electron microscopy of the etched characteristic surfaces of the preferred cleavage planes of TS single crystals[36,138,139] revealed specific ellipsoidal pits, caused by dislocations, arranged in certain preferred directions having a long axis in the [010] direction, which subsequently becomes the direction of the principal PDA chain. Photographs and schemes for different types of the observed defects have been published[138,139] and the possible role of active centres (chain propagation initiators) has been discussed. Thermal polymerisation, in which dislocations play an important role, then begins at localised sites corresponding to the centres of the elliptical pits, while all the polymer chains grow in only one direction—"plus" or "minus" depending on the sign of the Burgers vector of the dislocation lines. This hypothesis is confirmed by the additional appearance near the deformation zones of numerous characteristic dislocations, which arise as a consequence of the compression of TS in the [010] direction and at which polymerisation begins.[36,139] Evidence for the occurrence of localised polymerisation either at the dislocation sites or at the sites of macroscopic deformation, for example, scratches,

has not been obtained for a photoinitiated reaction. Thus the defects do not control the photopolymerisation, since each absorbed photon of energy should lead to reaction regardless of the presence of defects in the crystal.[138,139] As a consequence of this, the energy of the photon initiating the topochemical polymerisation (~370 kJ mol^{-1}) should be much higher than the energy stored in the dislocation centres (not more than 90–180 kJ mol^{-1} according to calculations) and should be comparable to the activation energy for thermal polymerisation (80–120 kJ mol^{-1}).[139]

All the PDA crystals synthesised are cleaved in specific directions. For example, HDDU is cleaved along the (100) and (102) planes, forming smooth surfaces suitable for spectroscopic and electrophysical studies. Various types of dislocations have been observed on these surfaces although it is not clear whether they appear in the course of cleavage, or whether they are already present in the single crystal, or whether they arise in the course of the topochemical polymerisation.[138] Detailed microscopic studies of single crystals of poly-TS taking into account the crystal structure[35,36,138–140] permitted the solution of a number of problems: a scheme has been devised for the slip systems, deformation twinning of the crystals has been observed, and the characteristics of the distribution of the polymer chains and defects in the single crystals have been determined. The results of studies of the morphology of poly-TS in a number of investigations have been examined critically.[141]

The structure of the dislocations in TS and poly-TS has been investigated in detail with the aid of Laue diagrams. The growth of dislocations in the TS crystal during topochemical polymerisation and the influence of dislocations on the polymerisation process have been analysed.[142] The characteristic features of the optical spectra of a specially synthesised high-defect poly-TS have been attributed to the presence of dislocations at which short polymer chains have been terminated.[143] It is believed[144] that dislocations are present in the TS crystals and are then fixed during polymerisation, affecting the topochemical polymerisation process and mechanical and electrical properties. For example, the anisotropy of the mobilities of the current carriers in the direction of the polymer chains and at right angles to them is associated with the one-dimensional character of the PDA. However, the difference between the ratios of the corresponding mobilities $\mu_\parallel/\mu_\perp$, which are 10 [145] and $(8 \pm 3) \times 10^2$,[146] can be attributed to dislocations.

Furthermore, the mobilities of current carriers $\mu_\parallel$, determined in different studies, differ in magnitude (1 – 5 $cm^2 V^{-1} s^{-1}$,[147–149] 6×10^3 $cm^2 V^{-1} s^{-1}$,[150] and 2×10^5 $cm^2 V^{-1} s^{-1}$ [151]) and can also be attributed to different contents of dislocations functioning as current carrier traps.[144] Indeed the edge dislocations in poly-TS with the Burgers vector parallel to the direction of the chain are present in an amount of 10^{13} m^{-2}.[144] An approximate calculation showed the following: if each dislocation (with a density of 10^{12}–10^{13} m^{-2}) disrupts a chain when the chain passes through a dislocation nucleus, the length of the undeformed section of the chain is 0.1 – 1 mm, which corresponds to the distance traversed by an electron in poly-TS.[151] Dislocations can be arranged in lines at right angles to the direction of the chain. When the density of the dislocations along the line become sufficiently great, low-angle grain boundaries are formed.[144]

Fibrillar crystals with a diameter not exceeding 1000 Å and having a length of several μm have been obtained by the crystallisation from solution of partly polymerised TS. The direction of the molecules in the crystals have not been determined, but it has been noted that the crystal structure of fibrillar crystals differs from that of lamellar crystals obtained by the polymerisation of DA single crystals.[152,153]

The conversion into an amorphous form of the poly-TS crystals formed by forging and rolling is not caused by chemical changes but is due to the chain defects (loops and bends), leading to the appearance of segments with different conjugation lengths along the chain.[154,155]

The deformations along the crystal lattice defects have been discovered with the aid of asymmetric high-resolution X-ray topography in DA and PDA with $R = (CH_2)_4OCONHC_6H_5$. The defects are preserved in the course of topochemical polymerisation and the degree of deformation along them does not increase.[156]

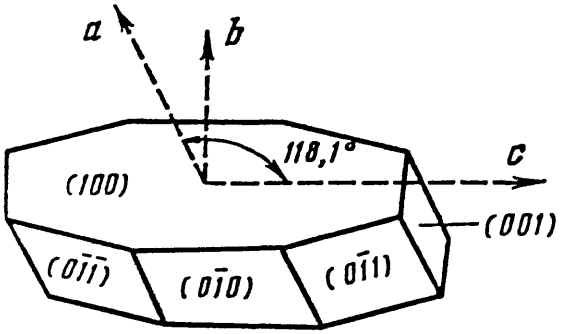


Figure 6. A TS crystal for dilatometric measurements; the (010) and (001) surfaces have been obtained by polishing.[108]

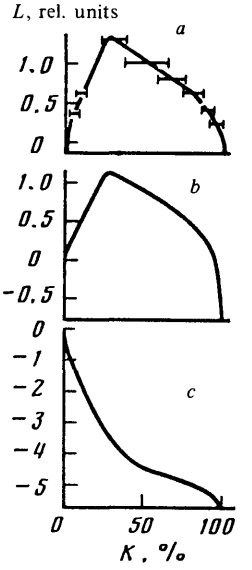


Figure 7. Variation of the dimensions L of a TS crystal with the degree of conversion K: *a*) $100\Delta d_{(100)}/d_{(100)}$; *b*) $100\Delta d_{(001)}/d_{(001)}$; *c*) $100\Delta b/b$.

The presence of a well formed TS crystal made it possible to investigate dilatometrically the kinetics of thermal (at 333.2 K) topochemical polymerisation. Direct measurements of the geometrical dimensions of the crystal (Fig.6)[108] at 276 and 294 K on the basis of the formulae

$$\frac{\Delta d_{(100)}}{d_{(100)}} = \frac{\Delta a}{a} + \Delta\beta \cot \beta,$$
$$\frac{d\Delta_{(010)}}{d_{(010)}} = \frac{\Delta b}{b},$$
$$\frac{\Delta d_{(001)}}{d_{(001)}} = \frac{\Delta c}{c} + \Delta\beta \cot \beta$$

were used to calculate the varying unit cell parameters. The existence of maxima in the parameter a and c in the region of 30% conversion has been observed, while the parameter b diminishes continuously (Fig.7).[108] The continuous variation of the parameter b during topochemical polymerisation has also been noted in another study.[116] However, examination of the unit cell parameters derived from X-ray diffraction data showed that the thermal polymerisation of TS (59.4 °C) is accompanied by a jump in b for the unit cell in the region of the transition from the induction period in topochemical polymerisation to the autocatalytic stage (~15% conversion) with a corresponding alteration of the reaction rate constant from 4.8×10^{-7} to 1.6×10^{-4} s^{-1}.[157,158]

X-Ray diffraction analysis of the products of the low-temperature phototopochemical polymerisation of symmetrical DA with R = $(CH_2)_4OSO_2$– –CH_3, carried out at T = 110 K, revealed the homogeneous character of the polymerisation up to 20% conversion of the monomer.[159]

On the other hand, in the case of the γ-initiated topochemical polymerisation at 20 °C all the DCHD unit cell parameters vary in jumps (see above) in the range of conversions of the monomer 30–50%, which is believed[98,160] to be a consequence of a phase transition.

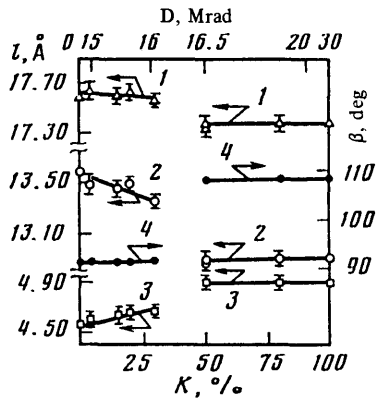


Figure 8. Variation of the parameters l of the DCHD crystal unit cell with the degree of conversion K and the γ-radiation dose D: 1) c; 2) a; 3) b; 4) β.[98]

The study of a poly-TS crystal by wide angle X-ray diffraction under a pressure $p \leq 16.5$ kbar revealed the variation of the parameters a and c as well as the angle β of the monoclinic unit cell with increasing pressure.[161] The compressibilities obtained have the following values:

Parameter	a	b	c	β
Compressibility, $kbar^{-1}$	$2.6 \cdot 10^{-3}$	0.0	$3.2 \cdot 10^{-3}$	$2.4 \cdot 10^{-4}$

The formation of PDA single crystals makes possible their complete X-ray diffraction analysis together with the calculation of the coordinates of all the atoms, the lengths of the valence bonds, and the angles, which means that one can determine the type of unit in the main chain. At the beginning of the development of the research into the solid-phase polymerisation, the isomorphism of the monomeric and polymeric crystals enabled the authors to regard the polymerisation process as one involving the rupture of two C≡C bonds via a mechanism involving the 1,4-addition of monomeric units to the polymer chain (Fig.1) with formation of an enyne (I) structure, or the cumulene (II) structure mesomeric relative to the former, which some workers[1-3,5,34,37] have found to be preferable.

However, calculations of bond length based on the results of the X-ray diffraction analysis of the HDDU,[84] TS,[162] and DCHD[163] polymers were found to agree better with the concept of the polymer chain as a flat zig-zag containing conjugated C=C and C≡C bonds. Not only in these but also in all other polymers investigated, the existence of only the *trans*-confugurations of a macromolecule relative to the C=C bond has been noted. Later X-ray diffraction analysis showed that the cumulene structure makes a greater contribution at least for PDA with R = $(CH_2)_4OCONHC_6H_5$ and for BPG.[164-166] Crystallographic data for a series of DA and PDA as well as the bond lengths in the PDA main chains are listed in Table 3.

Differences have been detected between the expansion coefficients of a crystal of a BPG monomer and the polymer chain in the study of the temperature variation of the position of the maximum in the electronic transition.[181]

The study of the reflection spectra of PDA with R = $(CH_2)_4$.$OC(O)NHC_2H_5$ deposited on ceramic discs with a high thermal expansion coefficient revealed a phase transition between liquid helium temperature to room temperature, induced by the removal of mechanical stress and accompanied by the structural change (II) → (I).[182] The thermochromic transition (green → red) observed for the same PDA at temperatures in the range 115–130 °C has been explained by a first-order phase transition accompanied by the structural change (I) → (II). The reverse process occurs in the region of 70 °C.[60]

A phase transition, caused by a rearrangement of the side groups at 142 K, has been observed for a carbazolyl-containing PDA with the aid of ultraviolet and Raman spectroscopy.[71]

X-Ray diffraction studies on poly-TS crystals revealed a reversible second-order phase transition below 170 K. The unit cell of the high-temperature phase

($P2_1/c$, a=14.493; b=4.910, c=14.930 Å; β=118.14°; Z=2)

contains two symmetrically arranged polymer chains extended along the b direction.[162] The transition to the low-temperature phase is characterised by the rotation of the side group in the neighbouring polymer chains in the opposite directions. Although the bond lengths and angles in the main chain are not altered in this process, two varieties of polymer chains appear in the unit cell and the latter is in fact doubled without change in the perfection of the single crystal

($P2_1/c$; a=14.92; b=4.910; c=25.56 Å; β=92°; Z=4).

The low-temperature splitting in the optical and Raman spectra of poly-TS has been explained by the existence of two types of polymer chain.[183-187] The monomeric TS undergoes two phase transitions.[158]

Table 3. Crystallographic data for DA and PDA.

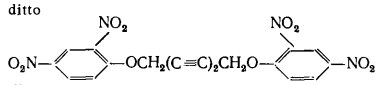
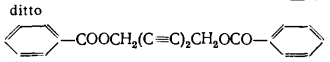
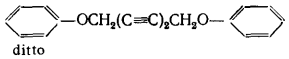
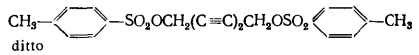
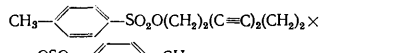
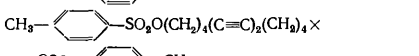
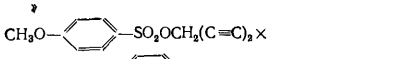
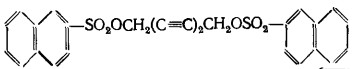
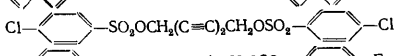
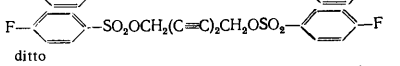
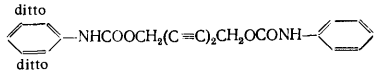
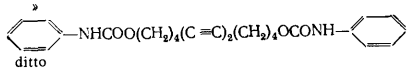
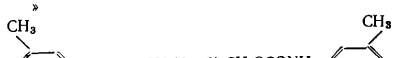
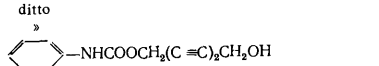
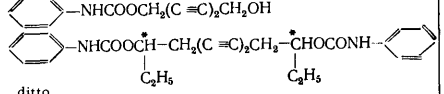
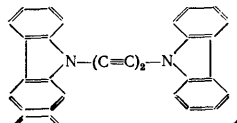
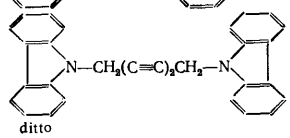
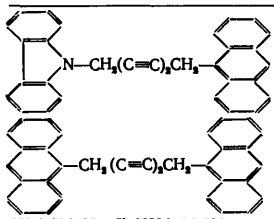
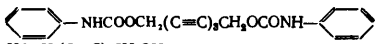
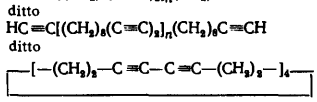
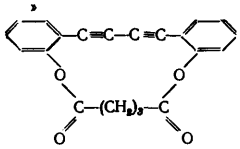
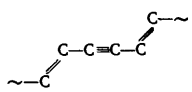
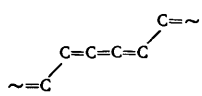
Monomer	DA or PDA	Unit cell parameters				Z	Space group	Factor R	Crystal system	Bond length (Fig.1), Å			Refs
		a, Å	*b*, Å	*c*, Å	β, deg					*A*	*B*	*C*	
$HOCH_2(C{\equiv}C)_2CH_2OH$	DA[1]	4.08	15.99	4.76	106.5	2	$P2_1/c$	—	monocl.	—	—	—	[92]
ditto	DA[1]	4.093	16.028	4.74	106.34	2	$P2_1/c$	—	ditto	—	—	—	[27]
»	PDA	4.176	15.785	4.703	110.34	2	$P2_1/c$	—	»	—	—	—	[27]
$HOCH_2CH_2(C{\equiv}C)_2CH_2CH_2OH$	DA	4.847	19.58	8.130	95.41	4	$P2_1/c$	0.042	»	—	—	—	[94]
$HOCH_2(C{\equiv}C)_2CH_3$	DA_2	4.893	28.471	4.131	101.67	4	$P2_1/c$	—	»	—	—	—	[93]
ditto	DA^2	4.375	28.117	4.028	102.24	4	$P2_1/c$	0.13	»	—	—	—	[93]
	DA	5.194	11.942	14.745	98.45	2/*m*	$P2_1/c$	—	»	—	—	—	[77]
ditto	PDA	4.930	11.977	14.877	95.09	2/*m*	$P2_1/c$	—	»	1.205	1.410	1.471	[77]
	DA[1,3]	14.02	4.352	15.14	118.9	2	$P2_1/c$	0.064	»	—	—	—	[96]
ditto	DA[1]	9.665	8.479	11.03	114.0	—	$P2_1/c$	0.085	—	—	—	—	[96]
	DA[1]	11.179	14.979	8.527	—	4	P_{cab}	—	orthorhomb.	—	—	—	[95]
ditto	DA	7.469	11.368	8.591	109.42	2	$P2_1/c$	—	monocl	—	—	—	[95]
	DA	14.60	5.15	15.02	118.4	2	$P2_1/c$	—	ditto	—	—	—	[35]
ditto	PDA[4]	14.93	4.91	25.56	92	4	$P2_1/c$	0.10	»	—	—	—	[167]
»	PDA	14.493	4.910	14.936	118.14	2/*n*	$P2_1/c$	0.055	»	1.191	1.428	1.356	[162]
	DA^1	7.034	9.590	9.692	111.7	1	—	0.055	tricl.	—	—	—	[168]
	DA	20.60	11.79	5.19	89.3	—	—	—	ditto	—	—	—	[90]
ditto	PDA[5]	20.13	6.11	4.91	93.7	—	—	—	»	—	—	—	[90]
»	PDA[5]	20.01	6.02	4.91	93.7	—	—	—	»	—	—	—	[90]
	DA^1	9.875	10.226	5.798	76.92	1	—	0.045	»	—	—	—	[91]
	PDA	4.902	8.543	12.724	77.220	1	—	—	»	1.223	1.400	1.265	[169, 170]
	DA^1	13.446	5.421	15.903	100.96	2	—	0.054	monocl.	—	—	—	[51]
	DA^1	8.941	11.170	5.030	91.19	1	—	0.045	tricl.	—	—	—	[86]
	DA	13.94	5.18	14.09	114.1	2	—	—	monocl.	—	—	—	[47]
ditto	PDA	13.93	4.90	14.06	113.3	2/*n*	—	—	ditto	—	—	—	[47]
	$PDA^{1,6}$	23.5	7.86	18.82	94.5	8	—	—	»	—	—	—	[10]
ditto	PDA[7]	4.89	12.53	16.78	96.81	—	$P\bar{1}$	—	»	1.21	1.41	1.36	[84]
»	DA^8	23.51	7.80	18.47	94.0	8	$C2/c$	0.065	»				[171, 172]
	PDA	6.229	39.027	4.909	106.85	4	$P2_1/c$	—	»	1.17	1.38	1.45	[101]
ditto	PDA	»	»	»	»	4	»	0.081	»	1.24	1.37	1.44	[57,166]
»	DA^8	18.97	5.19	11.60	92.0	4	$P2_1/c$	0.09	»	—	—	—	[171, 172]
	DA^1	21.908	9.982	9.352	108.03	4	$C2/c$	0.078	»	—	—	—	[85]
$CH_3CH_2NHCOOCH_2(C{\equiv}C)_2CH_2OCONHCH_2CH_3$	DA	16.82	17.72	4.70	96.6°	4	$P2_1/a$	—	»	—	—	—	[98]
ditto	DA^1	9.39	17.84	8.64	105°	4	$P2_1/a$	—	»	—	—	—	[98]
»	PDA	15.14	17.96	4.88	98.42°	4	$P2_1/a$	—	»	—	—	—	[98]
	PDA	38.77	23.64	4.86	—	16	$P_{na}2_1$	—	orthorhomb.	—	—	—	[87]
	DA	45.982	10.879	9.601	—	8	P_{bca}	—	ditto	—	—	—	[173]
ditto	DA	5.181	36.629	6.827	113.17	2	$P\bar{2}_1/c$	—	monocl.	—	—	—	[173]
	DA^1	15.306	13.742	4.656	—	2	$P2_12_12_1$	—	orthorhomb.	—	—	—	[97]
	DA^{10}	13.38	4.20	18.44	92	4	$P2_1/c$	0.13	monocl.	—	—	—	[99, 160]
ditto	DA	13.60	4.55	17.60	94	4	$P2_1/c$	0.13	ditto	—	—	—	[99, 160]
»	PDA	12.865	4.907	17.403	108.3	4/*n*	$P2_1/c$	0.086	»	1.21	1.44	1.33	[163]

Table 3 (contd.).

Monomer	DA or PDA	Unit cell parameters				Z	Space group	Factor R	Crystal system	Bond length (Fig.1), Å			Refs.
		a, Å	b, Å	c, Å	β, deg					A	B	C	
	DA	14.33	4.36	18.00	91.1	4	$P2_1/c$	0.09	»	—	—	—	[99]
	DA	14.60	4.35	17.92	97.0	4	—	0.098	»	—	—	—	[99]
$CH_3(CH_2)_8(C{\equiv}C)_2(CH_2)_8COOH$	DA	4.76	5.42	42.30	90	—	—	—	»	—	—	—	[102]
$CH_3(CH_2)_{11}(C{\equiv}C)_2COOH$	DA	4.91	5.36	32.7	91.6	2	$P\bar{1}$	—	tricl.	—	—	—	[174]
ditto	DA^{11}	4.77	7.09	33.2	91.6	3	$P\bar{1}$	—	ditto	—	—	—	[174]
$CH_3(CH_2)_{12}(C{\equiv}C)_2COOH$	DA^{11}	4.74	7.15	36.4	92.1	—	—	—	—	—	—	—	[174]
ditto	PDA^{11}	4.866	7.066	34.34	94.8	—	—	—	—	—	—	—	[174]
$HOCH_2(C{\equiv}C)_2CH_2OH$	polymer	4.11	19.59	4.80	109	2	$P2_1/c$	—	monocl.	—	—	—	[175]
	polymer	24.65	30.74	4.89	92.2	8	$P2_1/c$	—	ditto	—	—	—	[175]
$HOCH_2(C{\equiv}C)_4CH_2OH$	monomer	4.005	23.00	4.73	106.08	—	$P2_1/c$	—	»	—	—	—	[87]
$HC{\equiv}C[(CH_2)_5(C{\equiv}C)_2]_n(CH_2)_5C{\equiv}CH$	nDA^{12}	7.88	21.00	5.67	90.8	—	$P2_1$	—	»	—	—	—	[176]
ditto	PDA^{13}	4.65	17.5	4.85	101.7	—	$P2_1/n$	—	»	—	—	—	[176]
$HC{\equiv}C[(CH_2)_8(C{\equiv}C)_2]_n(CH_2)_8C{\equiv}CH$	nDA^{12}	13.25	14.15	7.63	118.5	—	$P2_1/n$	—	»	—	—	—	[176, 177]
ditto	PDA^{13}	9.17	12.25	9.92	123.5	—	$P2_1/n$	—	»	—	—	—	[176, 177]
	DA	24.54	4.98	25.38	93.2	4+1	C2, Cm or C2/m	—	»	—	—	—	[178]
ditto	PDA	12.43	4.8	25.34	—	2+2	—	—	orthorhomb.	—	—	—	[178]
»	PDA^{14}	12.05	4.8	25.23	—	—	—	—	—	—	—	—	[178]
»	PDA	12.4	4.8	24.8	—	2+2	Pgg	—	orthorhomb.	—	—	—	[179]
	DA	22.66	7.88	9.85	108.0	8	C2/c	0.078	monocl.	—	—	—	[88]
	DA^1	21.68	13.83	5.42	90.17	4	$P2_1/n$	0.062	ditto	—	—	—	[88]
ditto	PDA	23.12	7.87	9.69	111.29	4	C2/c or Cc	0.075	»	1.29	1.38	1.42	[57, 164, 166]
»	PDA	20.8	8.0	9.7	106	4	2C/c or Cc	—	»				[103]
	calculation for the ideal enyne PDA chain									1.20	1.45	1.34	[180]
										1.21	1.43	1.34	[84]
	calculation for the ideal cumulene PDA chain									1.26	1.35	1.48	[180]
										1.28	1.32	1.46	[84]

Remarks: [1]The monomer is inactive or its activity is low. [2]T = 110 K. [3]Polymerises at high pressure. [4]T < 170 K. [5]T = 110 K. [6]Crystallised from anisole. [7]Crystallised from the dioxan–water system. [8]T = 120 K. [9]The angle γ is quoted. [10]T < 142 K. [11]2:1 complex with phenazine. [12]Macromonomer. [13]Cross-linked macromonomer. [14]Polymer washed free of monomer.

The study of the polymerisation of TS led to the hypothesis[38] that the structure (II) obtains in the polymer for a low degree of conversion owing to the discrepancies between the unit cells of the monomer and polymer in the direction of the chain (the TS chain should increase in length by ~5%). The absorption spectra of TS at low conversions resemble those of PDA having the cumulene structure (II).[56] With increase of the degree of conversion, the strain energy diminishes and the enyne structure (I) becomes preferable. The induction period is then replaced by the autocatalytic stage involving an increase of the topochemical polymerisation rate constant by a factor of 100–400.[36,112,113] It is expected that only enyne structures are formed in the autocatalytic stage, while the cumulene structures are converted into the enyne structures. The consecutive transition of the structures is confirmed by the results of optical and EPR spectroscopic measurements.[130,155]# The results of the investigation of poly-TS by resonance Raman spectroscopy can apparently be accounted for by the contributions of different types of structures.[137] It has been suggested that, apart from the main *trans*-structure, there is another impurity structure which consists of a perturbed planar fully *trans*-structure and not a *cis*-structure.[137]

The majority of the workers who have investigated the optical infrared and Raman spectra of PDA have described the structure of their chains in terms of a mesomeric structure, the extreme manifestations of which are the cumulene and enyne units.[23,56,133] For example, in conformity with

#H.Gross and H.Sixl, Mol.Cryst.and Liquid Cryst., 1983, 93, 261.

the calculation for the Coulson and Dewar models, the fraction of the cumulene structure in poly-HDDU is 8–25% and diminishes when the chain conformation deviates from the planar zig-zag as a result of structural disorder.[23] The contributions of structures of different types depend on the chemical structure of the substituent in the monomer and also on the conditions in the preparation and state of the monomer whose variation can entail the reversible interconversion of these structures. However, regardless of the electronic structure of the chain, all the PDA have one common feature: a marked anisotropy of the physicochemical, electrolphysical, and other properties associated with the orientation of the polymer chain along the crystallographic *b* direction (Fig. 9).[7]

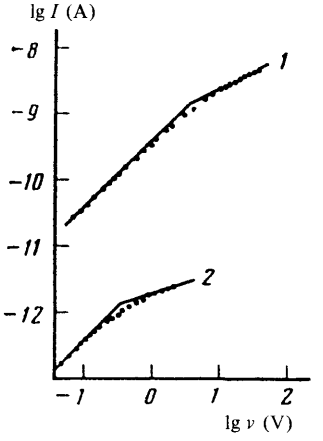
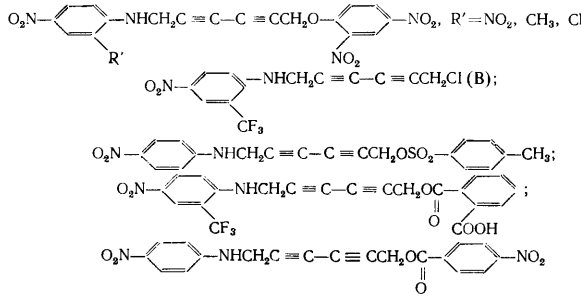


Figure 9. Variation of the photocurrent with the stress in a poly-TS single crystal; the light is polarised parallel (curve *1*) and at right angles (curve *2*) to the polymer chains (to the crystallographic *b* axis).[7]

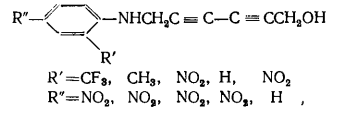
III. SPECIAL CASES OF THE SOLID-PHASE POLYMERISATION OF MONOMERS WITH $-(C\equiv C)_n-$ GROUPS

1. Polymerisation of Asymmetric Diacetylenes

A large number of polymeric single crystals have been synthesised from asymmetric DA of the type $R^1-C\equiv C-C\equiv C-R^2$ (Table 4). The study of the polymerisation of nitroanilino-substituted DA having the structure

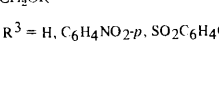
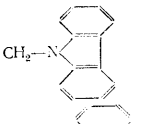
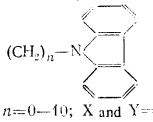


has shown that only the monomers (A) and (B) are reactive in the solid phase. The monomer (A) polymerises on heating and under the influence of ultraviolet radiation and X-rays, while the monomer (B) polymerises only under the influence of X-rays.[195] Among a series of asymmetric DA having the general formula



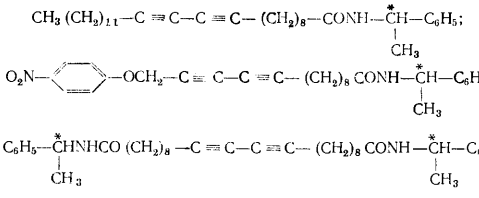
only those with $R' = CF_3$ and $R'' = NO_2$ polymerise under the influence of ultraviolet light and X-rays ($Cu K_\alpha$, 3 days, 73% conversion), although all the monomers are electronically and sterically similar.[196]

Table 4. The asymmetric DA $R^1-C\equiv C-C\equiv C-R^2$ investigated in the solid-phase polymerisation.

R^1	R^2	Refs.
CH_2OH	CH_3	[23,31,32,39,188]
$CH_2OCONHC_6H_5$	CH_3	[23]
$CH_2CH(C_2H_5)OCONHC_6H_5$	CH_3	[23]
$CH_2OCONHC_2H_5$	CH_3	[23,87]
$CH_2OCONHC_6H_5$	CH_2OH	[87]
$CH_2OCONHC_6H_5$	$CH_2OCONHCH_3$	[87]
COOH	$(CH_2)_{11}CH_3$	[133]
$(CH_2)_8COOH$	$(CH_2)_9CH_3$	[32,102,189–192]
$(CH_2)_nCOOH$	$(CH_2)_nCH_3$	
	$n = 4,7,11,13,15$	[190,191,193]
CH_2OR^3	CH_2OR^4	
R^3 = H, $C_6H_4NO_2$-*p*, $SO_2C_6H_4CH_3$-*p*	R^4 = 	[76]
CH_2Cl	CH_2O—	[76]
	$C_{12}H_{25}$	[74]
	$(CH_2)_nR^4$	[194]
$n = 0–10$; X and Y = H, Cl, Br, NO	$n = 0–10$; $R^4 = CH_3$, OH, $OCONHR^5$ (R^5 = Alk, Ar)	

Polymerisation in single crystals and monolayers of DA having the structures $CH_3(CH_2)_{17}C\equiv C-C\equiv CCOOM$ ($M = H^+$, Cu^+, or Ag^+) and $HC\equiv C-C\equiv(CH_2)_{17}COOH$ led to the formation of blue and red polymers respectively.[197] The instability of the copper salt in the crystalline state has been noted.

DA with chiral substituents, derivatives of *d*(+)-α-methylbenzylamine, are highly sensitive to ultraviolet light and X-rays:

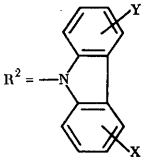


It has been observed that the asymmetric DA with the $CH_3(CH_2)_{11}$ end groups has a higher quantum efficiency (1×10^{12}) than the corresponding pentacosa-10,12-diynoic acid (1.6×10^{11}). It has been suggested that it be used to cross-link polymeric materials (for example glycidyl methacrylate) and also in photography and lithography.[198]

Carbozole-containing polymers based on the monomers

$$R^1(CH_2)_mC{\equiv}C{-}C{\equiv}C(CH_2)_nR^2,$$

in which m and n = 0–10 and $R^1 = CH_3$, OH, OC(O)NHR^3 [R^3 = alkyl (C_1–C_{18}), phenyl, tolyl, naphthyl, or $CH_2OC(O)C_qH_{2q+1}$ (q = 2–4)] have been proposed as materials with non-linear optical properties:[194]



X and Y = H, Cl, Br, NO_2.

The photopolymerisation of the tetrachlorocadmates $(RNH_3)_2CdCl_4$ (where R = $CH_2C{\equiv}CC{\equiv}CCH_2Cl$) with organic cations is known.[199] The use of asymmetric DA containing simultaneously hydrophilic and hydrophobic substituents made it possible to obtain and investigate polymeric monolayers and multilayers with unique structures.[200]

Infrared spectroscopic study of the blue products of the polymerisation of hepta-2,4-diynoic acids[133] (^{60}Co γ-radiation: 120 Mrad; 0.135 Mrad h^{-1}) showed that during solid-phase polymerisation a single crystal contains three components (the monomer, the insoluble polymer, and a segregated soluble oligomer), which give rise to two individual solid solutions over the entire range of conversions: the phase enriched in the monomer [with frequencies 1420, 905, and 600 cm^{-1} for the $(CH_2)_n$ groups], which is converted into a phase enriched in the polymer [with frequencies 1350 and 835 cm^{-1} for the $(CH_2)_n$ groups]. It is of interest that the authors proposed a cumulene structure of the chain unit for the intermediate oligomer.

The presence of two different non-chiral substituents in the monomeric molecule makes possible the existence of additional, compared with symmetrical diacetylenes, types of structure in the PDA molecules: "head to tail", "head to head", or both simultaneously. For the polymers obtained (using ^{60}Co γ-radiation) from the asymmetric diacetylenes

$$CH_3C{\equiv}C{-}C{\equiv}CCH_2OCONHC_6H_5;\ HOCH_2C{\equiv}C{-}C{\equiv}CCH_2OCONHC_6H_5;$$
$$CH_3NHCOOCH_2C{\equiv}C{-}C{\equiv}C{-}CH_2OCONHC_6H_5$$

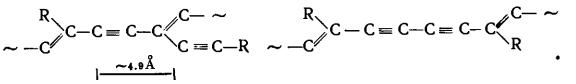
only the first type of addition has been observed with a regular alternation of "head–tail" side groups and the occurrence of entirely the *trans*-conformation in the polymer chain.[87]

Being formally symmetrical, a DA having chiral groups can give rise to several types of addition of units. The mixture of the DA $R{-}C{\equiv}C{-}C{\equiv}C{-}R$, $S{-}C{\equiv}C{-}C{\equiv}C{-}S$, and $R{-}C{\equiv}C{-}C{\equiv}C{-}S$ [R and S are the chiral groups $-CH_2\overset{*}{C}H(CH_2CH_3)-OCONHC_6H_5$ of different sign], synthesised by Wilson et al.,[173] crystallises in two crystallographic modifications one of which is a racemic mixture, while the other is optically inactive. Their polymerisation leads to the corresponding PDA having the structures $[{=}C(R)C{\equiv}CC(R){-}C(S)C{\equiv}CC(S){=}]_n$ and $[{=}C(R)C{\equiv}CC(S){=}]_n$.

Certain general criteria of the solid-phase polymerisation of asymmetric diacetylenes have been stated by Baughman and Yee.[87]

2. Polymerisation of Linear Monomers with the $-(C{\equiv}C)_n-$ Groups

The polymerisation of triynes having the general formula $R{-}(C{\equiv}C)_3{-}R$ can proceed via a 1,4-addition reaction with formation of asymmetric side substituents R and $C{\equiv}C{-}R$ and via the 1,6-addition reaction with formation of symmetrical substituents R or, via a combination of both processes:



Examination of the MMAD principle in relation to triynes demonstrated a higher probability of the formation of fully *trans*-polymers in the case of both 1,4- and 1,6-addition than that of the formation of the corresponding *cis*-polymers. Furthermore, it has been noted that higher MMAD are required for the 1,6-addition reaction than for the 1,4-addition.[87] It must be emphasised that the polymer formed can have the type of symmetry corresponding to the monomer type of symmetry, which agrees with the specificity of both the 1,6-addition reaction of triynes and the 1,4-addition of symmetrical diynes. However, for the topochemical asymmetric 1,4-addition reaction of triynes, which should be preferred in conformity with the MMAD principle, the monomer type of symmetry corresponding to the possible occurrence of such topochemical polymerisation is 1 or m, which has in fact been observed.[87] The absence of the topochemical polymerisation of dimethyltriacetylene, the molecular symmetry of which ($\bar{3}m$) [81,201] rules out the occurrence of a specific reaction of this monomer via both 1,4- and 1,6-additions in agreement with the criteria concerning the type of symmetry formulated above.

Table 5. Polymerisation of the triynes $R{-}(C{\equiv}C)_3{-}R$.[193]

R	Photopolymerisation[1]		Thermal polymerisation		
	yield[2] of polymer	colour[3]	T, °C	τ, h	yield of polymer, %
CH_2OH	+++	purple-red	60	52	87
			100	0—1	—[4]
$CH_2OCONHC_6H_5$	+++	dark-blue	60	50	6—7
			70	70	14
			100	22	71
$CH_2OCONH(CH_2)_5CH_3$	++	blue	70	70	0
$CH_2OCOC_6H_5$	+	brown	100	20	88
$CH_2OSO_2C_6H_4$ (p-CH_3)	++	violet	70	70	0
			83	40	—[5]
			100	1	—[5]

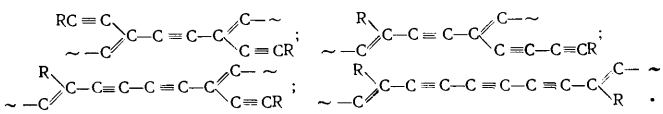
Remarks. [1]Moderate-pressure mercury lamp, room temperature, 3 h. [2]– = no polymerisation, + = low yield (<1%), ++ = moderate yield (<10%), +++ = high yield (>20%). [3]Unresolved polymer–monomer mixture. [4]Rapid carbonisation takes place. [5]Elimination of sulphonate groups (according to infrared spectroscopic data).

Examination of the polymerisation reactivity of octa-2,4,6-triyne-1,8-diol and some of its derivatives in topochemical polymerisation showed that the diol is the most reactive monomer (it polymerises readily even on recrystallisation in the dark at room temperature). The diphenylurethane of the diol polymerises to a crystalline polymer on heating and also on irradiation with ultraviolet light and X-rays, but its reactivity is lower. The dibutylurethane and the dibenzoate

are inactive in the photochemical reaction, although heating of the dibenzoate at 100 °C gives rise to a black polymer in 88% yield. On the other hand, the bistoluenesulphonate is photochemically reactive but does not undergo thermal polymerisation. The reactivity of triynes in photopolymerisation thus diminishes in the sequence diol > phenylurethane > toluenesulphonate > butylurethane > benzoate, the most reactive form of the phenylurethane derivative having been obtained by recrystallising the monomer from a petroleum ether–benzene mixture (Table 5). Triynes with large α-substituents [R = $C(CH_3)_2OH$] do not photopolymerise.[175]

Depending on the structure of the macromolecules, the repeat period of the chain may range from 1 (~4.9 Å) to 4 (19.6 Å) monomer units. The study of the structure of the polymers synthesised (Table 3)[87,175] showed that *trans*-polymerisation does indeed take place fully, while 1,4-addition with formation of structure (I) in the topochemical polymerisation of the biphenylurethane of octatriynediol leads to a crystalline polymer, while the polymerisation of octatriynediol up to a high degree of conversion results in a polymer with a perturbed three-dimensional order.

In the polymerisation of tetraynes the PDA chains can have four types of units and can also consist of a combination of two or more structures:

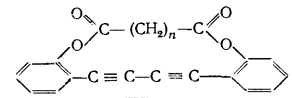


in the presence of asymmetric substituents in the main PDA chain [for example, R and RC≡C] there is a possibility of the "head to head" and "head to tail" addition of the monomer molecules which increases the number of possible variants of the polytetrayne structure. The structure becomes still more complicated when the substituents possess optical activity.

According to infrared and Raman spectroscopic and X-ray diffraction data (Table 3), the symmetrical tetrayne with $R=CH_2OCONHC_2H_5$ polymerises thermally and under the influence of γ-radiation without changes in the side groups forming the polymeric skeleton $(=RC-C\equiv C-CR'=)_n$, in which the length of the repeating fragment is 4.75 Å. Nevertheless it has not been established whether symmetrical polymerisation with formation of C≡C–R side groups or asymmetric polymerisation with formation of the R and $C\equiv C)_2$–R side groups takes place.[87] X-Ray diffraction has shown that the unit cell parameters vary gradually during the reaction with increasing degree of conversion and that a new phase does not appear. Such absence of phase separation is a necessary condition for the solid-phase synthesis of polymeric single crystals. However, the three-dimensional order of the monomeric phase is not retained in the polymer from which the monomer has been extracted and depends on the method of initiation of the reaction: the γ-initiated reaction leads to an amorphous polymer with extended chains, while the thermal reaction results in the formation of a polymer having two-dimensional order but a perturbed periodicity in the direction of the chain.[87] The γ-initiated topochemical polymerisation of the symmetrical diol $HO-CH_2-(C\equiv C)_4CH_2-OH$, which crystallises as an isomorphous phase with triacetylenic and diacetylenic diols, breaks up the three-dimensional order in the monomeric phase. This results in the formation of a monomer having an extended chain in which the repeating fragment is 4.9 Å long, in good agreement with the 1,4-addition of the monomer molecules involving the formation of a fully *trans*-polymer.[87]

3. Polymerisation of Cyclic Monomers

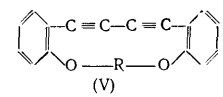
The synthesis of cyclic compounds containing conjugated C–C bonds established that some of these compounds are just as unstable in the solid phase as linear diacetylenes although they are fairly stable in solutions.[202–204] In both cyclic and linear diynes, the structure of the substituents R has been found to have a stong influence on the reactivity of the monomer.



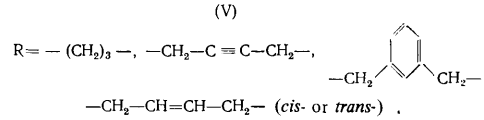
(IV)

$n = 3, 4, 5, 7$.

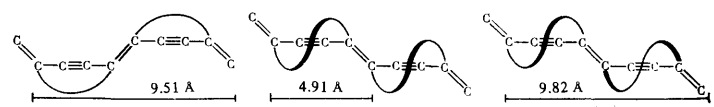
Monomers of type (IV) are sensitive to light only for $n = 3$.[202] The strongly strained ethers (V) are fairly stable in the solid state under illumination but are sensitive to heating:[203]



(V)



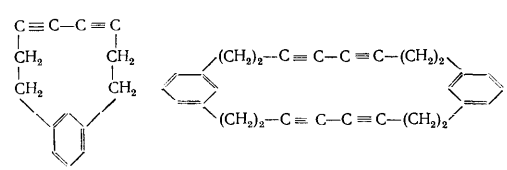
The polymerisation of *oo*-buta-1,3-diynylenediphenyl glutarate (BPG) (IV) ($n = 3$) under the influence of ultraviolet light or γ-radiation affords, after the extraction of the monomer which failed to react, an asbestos-like infusible insoluble PDA in yields up to 35–40%.[57,103,164,181] The non-extracted product of the polymerisation reaction is a solid solution of the polymer in the monomer matrix, the axis of the monomer being rotated by 33° in the course of the topochemical polymerisation and the side groups undergoing a change in orientation. The structure of poly-BPG can be represented by the following units:



(VI)

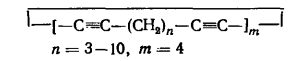
It has been established by X-ray diffraction (Table 3), optical dichroism, and infrared and Raman spectroscopy[103,164,205] that the macromolecules consist of a flat zig-zag (fully *trans*-polymer) with helically coiled substituents [structure (VI)]. The repeating interval in the achiral chain then consists of a double unit (~9.7 Å), which is satisfactorily consistent with calculations carried out taking into account the valence angles and bond lengths (9.82 Å).[103] Studies have shown[103, 181,206] that the polymer contains conjugated C≡C– and C≡C– (*trans*) bonds, although there is a possibility of a contribution by the cumulene structure.

The exceptionally unstable compound (VII) polymerises in several seconds to give an insoluble red polymer even in the dark, while the cyclic compound (VIII) is stable.[203]



(VII) (VIII)

The macrocyclic compounds (IX) have been proposed for the synthesis of three-dimensional polymers having fully conjugated parallel chains and hence exhibiting a strong dichroism.[207]



(IX)

The ladder polymers based on compound (IX) should have had higher moduli of elasticity and thermal stabilities than the linear PDA.

The study of a series of cyclic monomers (IX) ($n = 4$, $m = 2$–4), obtained by the oxidative dehydrocondensation of octa-1,7-diyne,[208] showed that the monomer with $m = 4$ exhibits the greatest capacity for topochemical polymerisation. Crystalline modifications both photochemically inert and reactive polymerising under the influence of γ-radiation, ultraviolet light, heat, or mechanical action, with formation of pink polymeric crystals, have been obtained from different solvents.[179,208] Elemental analysis has shown that the "active" form crystallises with inclusion of 1 mole of chloroform per cyclotetrameric unit. It is of interest that the "inactive" crystals contain 1 mole of benzene per mole of the cyclotetramer according to infrared spectroscopic and ^1H NMR data. When the "active" colourless acicular crystals are kept in the dark *in vacuo*, chloroform is removed and the crystals are converted into a yellow amorphous modification with a melting point close to that of the monomer but do not undergo solid-phase polymerisation. Accordingly, it is recommended that the monomer be polymerised under pressure of chloroform vapour in order to prevent the evaporation of chloroform from the single crystal. The infusible, insoluble polymer obtained retains the form of the crystals of the initial monomer and exhibits a strong dichroism with the dichroism axis parallel to the axis of the acicular crystal. According to Raman spectroscopic data, the polymerisation occurred as a 1,4-addition reaction of the diacetylenic groups of the monomer.[179,207,208] The unit cell of the polymer incorporating two monomeric units and two chloroform molecules has the parameters $a = 12.4$ Å, $b = 24.8$ Å, and $c = 4.8$ Å, where c represents the direction of the polymer chain. Comparison of these results with molecular models made it possible to assume that the most preferred of the three possible conformations (crown, boat, and chair) is the chair conformation, which is less strained and has a repeat period of ~4.9 Å.[179]

The total insolubility of the polymerised specimen shows that the cyclotetramer polymerises (γ-radiation, 50 Mrad) quantitatively. However, the low degree of crystallinity (40%), the positive temperature coefficient of linear expansion, and a lower mechanical strength than that of the linear PDA showed that the polymer might have contained $-(C\equiv C)_2-$ groups which failed to react. It has been established that resonance Raman spectroscopy does not always make it possible to determine the degree of conversion of the monomer, since, for example, the characteristic band of PDA with $R = (CH_2)_3OCONHC_6H_5$ might not have been observed in the spectrum of a mixture containing 75% DA and 25% of its polymer. In addition, the DSC curve for the polycyclic compound revealed an exothermic peak with a maximum at 197 °C corresponding to the exothermic 1,4-addition reaction of the $-(C\equiv C)_2-$ groups which failed to react in the course of the polymerisation, whose heat overlaps the endothermic heat of evolution of the solvent.[179]

4. Polymerisation at High Pressure

Diacetylenes in the single crystals where the distances between the terminal carbon atoms of the C≡C bonds in neighbouring molecules are greater than a certain critical value do not polymerise. A factor promoting the polymerisation of such monomers is an increase of pressure. A typical example of DA which is difficult to polymerise is provided by HD dibenzoate, which crystallises in two forms which are and are not capable of polymerising under high pressure.[23,96] X-Ray diffraction studies of the two forms have shown that this is caused by a difference between the distances separating the carbon atoms in the C≡C bonds in neighbouring reacting molecules (4.02 and 5.36 Å respectively).[96]

The study of the solid-phase polymerisation of DPB, HD, and hexadiyne under a pressure of 75 kbar (the specimen was placed in a solid medium which transmitted the pressure) and at temperatures up to 260 °C showed that the smallest amount of polymer detectable at 21 °C after 1 h is obtained at minimum pressures of 60, 20, and 60 kbar respectively.[24] Assuming that the compressibilities of the monomer crystals are identical, the authors believe that the crystal lattices of the monomers are distorted in the course of topochemical polymerisation until the attainment of the structural parameters optimal for polymerisation. The polymers from which the monomer has been removed by extraction are amorphous. The remaining hydrogen bonds in the partly polymerised HD are disrupted on extraction of the monomer. The infrared spectra of PDA indicate the occurrence of 1,4-addition with formation of units of type (II) in poly-DPB and of type (I) in the HD and hexadiyne polymers. Ogo and Okuri attributed the same structure to poly-HD.[209]

The sterically hindered α-substituted DA, such as octa-3,5-diyne-2,7-diol and its bisphenylurethane and bistoluenesulphonate, become capable of polymerising with increase of pressure to 30 kbar. The yield of the polymers depends more on the pressure than on time and temperature. A structure of type (II) has been proposed for the main chain.[210]

Detailed study of the kinetics of the thermal topochemical polymerisation of TS under hydrostatic pressure[107,211] demonstrated the disappearance of the autocatalytic effect at a pressure $p \geq 2$–4 kbar. Since the autocatalytic effect has been attributed to the difference between the dimensions of the monomeric and polymeric crystals, the influence of pressure was explained by the equalisation of the monomeric and polymeric lattices with its aid; at $p = 1$ kbar the length of the repeating fragment in PDA single crystals is smaller by 0.25 Å (~5%) than in the monomer single crystals, while the corresponding length at $p \geq 4$–2 kbar is smaller by 0.1 Å.[211]

The photopolymerisation of TS, carried out in an optical cuvette under a hydrostatic pressure up to 4 kbar, and also the study of the resulting specimens by scanning electron microscopy showed that the size of the polymerised sections increases with increasing pressure.[122] The solid-phase polymerisation takes place along the entire surface of the crystal and breaks arise as a result of contraction in the direction of the chain. In the non-irradiated regions of the crystal, secondary chain initiation by the primary growing chains has been observed.

5. The Joint Crystallisation of Diacetylenes and Their Polymerisation

The photoinitiated polymerisation of DA take place when the single crystals are irradiated with light having a wavelength within the absorption band of the monomer. The photosensitised polymerisation of 2,4-diynoic acids $R^1-C\equiv C-C\equiv C-R^2$ [$R^1 = COOH$, $R^2 = (CH_2)_nCH_3$, $n = 11$, 13, or 15], cocrystallised with phenazine, has been reported.[174,212] Mixed crystals of DA and phenazine having the dimensions 10 × 2 × 0.5 mm have been obtained from an alcoholic solution

containing both substances by slow evaporation of the solvent. The crystals have the stoichiometric composition of a complex comprising two molecules of the diynoic acid and one phenazine molecule and exhibit the fluorescence observed for pure phenazine crystals. According to infrared spectroscopic data, there is no formation of a salt (?complex) of any kind between the diynoic acid and phenazine. Polymerisation takes place readily in the mixed crystals under the influence of visible light ($\lambda \leqslant 450$ nm), while the pure diynoic acid is not polymerised by light with $\lambda > 300$ nm. It has been noted that, when $\lambda = 400$–430 nm, the quantum yield ϕ of the sensitised photopolymerisation of the cocrystallised material is approximately 10 times smaller than the ϕ observed on direct irradiation of the acetylenic chromophore.[212] The rate of polymerisation of the pure acid is initially higher than that of the cocrystallised compound, but a lower limiting degree of conversion has been noted in the former case.[174]

The crystal structures of the acids and their cocrystallised mixtures with phenazine have been studied (Table 3), which has led to a model capable of explaining the characteristic features of the topochemical polymerisation of the acid and its complex. According to the model, the acid molecules are packed in the single crystals in layers of the "head–head–tail–tail" type (Fig.10). The authors[174] regard the crystal structure of the complex as intermediate between the structures of the pure compounds and explain thereby why acridine and pyrazine do not form analogous complexes. On the other hand, the 4,6- and 10,12-diynoic acids do not cocrystallise with phenazine, unlike the 2,4-diynoic acids, probably because the latter have a higher pK_a owing to the strong electron-accepting character of the $C\equiv C-C\equiv C$ group, which means that they have a greater capacity for the formation of complexes with phenazine. Phenazine is removed by extraction from the coloured polymeric crystals obtained by topochemical polymerisation, after which the latter assume a fibrous form. Other substances can be introduced into the space produced by the removal of phenazine.[174] In the PDA chains the monomer units are linked "head to tail".[174]

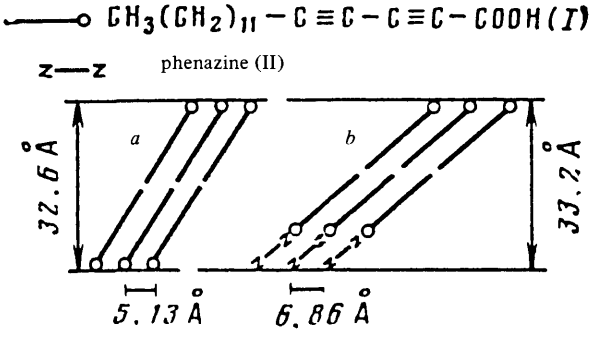


Figure 10. Structural models of DA (*a*) and of the cocrystallised DA–phenazine mixture (*b*) in the (100) projection i.e. at right angles to the direction of the PDA chains.[174]

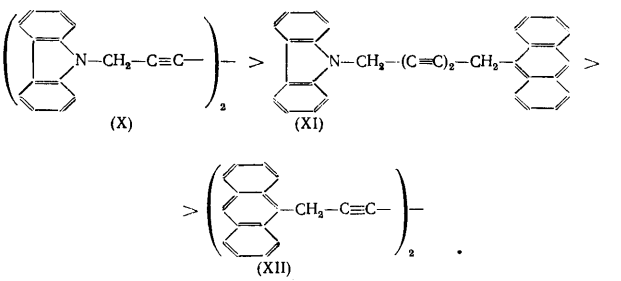
The study of the photoinduced topochemical polymerisation using the light corresponding to the optical excitation band of phenazine ($\lambda = 420$ nm) or DA ($\lambda = 280$ nm) revealed differences between the corresponding quantum yields ($\phi_{420} = 0.1$ and $\phi_{280} = 0.5$) and activation energies ($E_{420} = 0.21$ eV and $E_{280} = 0.17$ eV). It is believed that there is no electron transfer from the excited phenazine molecule to DA.[213]

Another aspect of the use of the mixed crystals is the solid-phase copolymerisation of various cocrystallising diacetylenic monomers, for example, those containing the urethane groups $R = CH_2OCONCH_6H_4X$, where X = H, *p*-Cl, or *p*-Br.[214] The relatively unreactive HD bis(*m*-trifluoromethylbenzenesulphonate) cocrystallises with the isomorphous TS. Thermal polymerisation of DA takes place in the jointly crystallised material, the duration of the induction period, which is also observed in the topochemical polymerisation of pure TS, depending on the ratio of the comonomers.[47,48]

It has been observed that the monomers (III) with R = *p*-Cl or *p*-CH_3 give rise to a series of mixed single crystals owing to the similarity of the van der Waals radii of the substituents Cl and CH_3.[215,216] The formation of solid solutions has been observed also for the symmetrical diacetylenes with $R = CH_2OCONHC_6H_5$ or CH_2OCONH-2-thienyl.[216] The diacetylene (III) with R = *p*-OCH_3 (there is no induction period[44,46,134,169,170]) and DA with R = naphthalene-2-sulphonyloxy (inactive in topochemical polymerisation[51]) also cocrystallise with TS, the composition of the crystals having been determined from the absorption spectra. Ideal solid solutions are formed when the content of the naphthalenesulphonates is 0–50%. The induction period in the topochemical polymerisation in the mixed crystals of TS with compound (III) (R = *p*-OCH_3) or DA with R = naphthalene-2-sulphonyloxy diminishes with decreasing fraction of TS in the crystal.[215]

It has been shown that the crystals produced by the cocrystallisation of TS and the inactive compounds (III) (where R = *p*-Cl [217,218] or R = *p*-Br [218]) form both reactive and unreactive modifications. A significant rearrangement of the TS crystal lattice does not occur when the content of the chloro-derivative is up to 20%, while in the mixed crystals of the bromo-derivative perturbations of the lattice are observed at lower concentrations of the latter as a consequence of the greater bulk of the bromine atom. The parameter *b* of the cocrystallised material diminishes monotonically with increasing content of the chloro- or bromo-derivative in the mixture with TS with a simultaneous decrease of the melting point. The copolymerisation of TS with compound (III) (R = *p*-Cl or *p*-Br) proceeds up to total conversion and is characterised by an induction period whose duration increases with increasing fraction of the inactive halogen-containing DA. However, in the case of the chloro-derivative an initial decrease of the induction period with increasing mole fraction of the chlorine-containing DA and the cocrystallised material in the range 0–0.05% has been observed, which is difficult to explain. The activation energy E_a for the copolymerisation reaction is identical with E_a for the homopolymerisation of TS, but the rate of topochemical polymerisation is lower than that for the pure TS.[218] Phase separation has never been observed in the course of topochemical polymerisation regardless of the composition of the cocrystallised material.[217,218] The comonomer units are distributed statistically.[218]

The capacity of DA with polynuclear aromatic substituents for polymerisation diminishes in the sequence[69,216]



The diacetylene (XI) undergoes thermal polymerisation (with decomposition) only near the melting point of the monomer and does not undergo radiation-induced polymerisation. The monomers (XI) and (XII) and certain DA derivatives of quinoline, phenothiazine, and acridine in various proportions cocrystallise with DCHD (X) (Fig.11), the mixed crystals polymerising not only thermally but also under the influence of γ-radiation. The ratio of the monomers in the non-polymerised cocrystallised material differs from that in the solution from which the crystal of the cocrystallised material has been grown. Compounds (XI) and (XII) have an inhibiting effect on the photoinitiated copolymerisation of compound (X) using light with λ = 250 and 350 nm, the wavelength corresponding to the absorption bands of the diacetylenic and carbazolyl fragments. When the crystals obtained by cocrystallising compound (X) with compound (XI) or (XII) are illuminated with light corresponding to the absorption band of the anthryl group (λ = 400 nm), the process is sensitised. This has been explained by the effective transfer of the excitation energy to the active centres in the crystals obtained by cocrystallisation.[99] As in the case of other types of cocrystallised crystals, the decrease of the fraction of the relatively inactive DA in the crystal obtained by crystallisation with an active DA [compound (X)][25,71] increases the rate of topochemical polymerisation with a simultaneous decrease of the induction period (Fig.12). This finding can be accounted for by the gradual approach by the parameter *b* of the crystal, along which the topochemical polymerisation takes place, to the optimum values characteristic of the pure compound (X) (Fig.11 and Table 2). Chemical and spectroscopic analysis of single crystals of the copolymers have shown that their composition is analogous to that of the initial comonomeric crystals.[99]

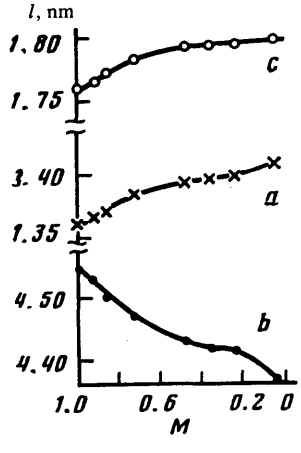
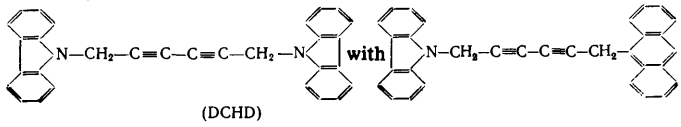


Figure 11. The influence of the DCHD mole fraction *M* in the crystal obtained by cocrystallising



(DCHD)

on the unit cell parameters.[99]

It has been observed that mixtures of different DA show a greater contrast in colour changes on heating or irradiation than the individual DA. The cocrystallised crystals of two and more linear or cyclic monomers of different structure have therefore been suggested as thermal indicators or γ-radiation dose indicators on the basis of changes over their colour range.[219]

The cocrystallised crystallisation and copolymerisation of symmetrical monomers of similar structure, namely DA with R = $CH_2OCONH(CH_2)_3CH_3$ and $CH_2OCONHCH_2CH_3$ as well as DA with R = $(CH_2)_2OH$ and $C(CH_3)_2OH$, have been investigated with the aid of optical spectroscopy and DSC.[220]

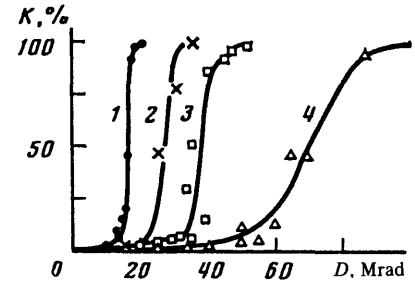
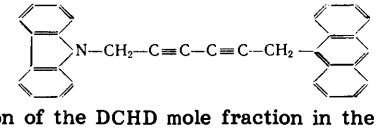


Figure 12. Dependence of the degree of conversion *K* on the dose *D* in the γ-initiated topochemical polymerisation of the cocrystallised mixture of DCHD and



as a function of the DCHD mole fraction in the cocrystallised material: 1) 1.000; 2) 0.989; 3) 0.978; 4) 0.945.[99]

IV. SOLUBLE DIACETYLENE POLYMERS AND THEIR PROPERTIES

The polymers obtained by the topochemical polymerisation of DA are as a rule insoluble in the usual organic solvents. However, it has been noted that many polymers based on the urethane derivatives of HD [2] and substituted DPB [5] dissolve in hexamethylphosphoramide (HMP). The polymers of 2,2-bis(acetamido)- and 3,3-bis(phenylureido)-diphenyldiacetylene dissolve in addition in concentrated sulphuric acid.[5]

Poly-TS dissolves in hot nitrobenzene, dimethylformamide (DMF), HMP, and butyrolactone, crystallising anew after the solutions have been allowed to stand.[37] The same polymer synthesised up to 12% conversion dissolves in DMF.[221] The yellow colour of the solution remains unchanged after reducing the temperature and adding the solvent. The electronic absorption spectrum of the solution has a broad maximum with $\lambda_{max} \cong 450$ nm and the extinction coefficient $\varepsilon = 5.6 \times 10^3$ litre mol^{-1} cm^{-1}, as well as a long-wavelength low-intensity downward slope. A gel permeation chromatogram demonstrated a broad molecular weight distribution (MWD) of poly-TS ($\bar{M}_n = 0.98 \times 10^5$, $\bar{M}_w = 4.80 \times 10^5$), it does not change as the degree of conversion increases to 12%, which demonstrates an increase in the number of oligomeric chains while their length remains unaltered. The average degree of

polymerisation of the soluble oligomer is $\bar{n} \cong 20$, while the chains with $\bar{n} \cong 100-200$, present in a small amount, are slowly precipitated at room temperature.[221] With increased degree of conversion of TS, the polymer chain length increases markedly. However, it is not clear whether this is a consequence of the growth of the chains formed during the induction period or whether it occurs as a result of the initiation of longer chains in the autocatalytic stage.

The results of a theoretical study of the thermal topochemical polymerisation of TS, which showed[157] that the growth of strained PDA chains is greatly hindered during the induction period (the rate constant is $k = 7.8 \times 10^{-7}$ s^{-1}), is in good agreement with experiment. Short chains [~100 Å ($\bar{n} = 20$)] are formed. After the attainment of a degree of conversion of ~15%, the chain length reaches 200 Å, In the autocatalytic stage ($k = 1.6 \times 10^{-4}$ s^{-1}) the length of the chains formed is greater than 700 Å.[222] An indirect estimate of the size of the poly-TS chains at high conversions of the monomer yielded the following values: $\bar{n} \cong 4200$ and a chain length $L \cong 2$ μm were found in a study of the kinetics of thermal topochemical polymerisation;[111] $100 < \bar{n} < 10000$ was found in a Brillouin scattering study;[116] $L \cong 5$ μm was found in an electron microscopic investigation of the etching profile of photopolymerised TS.[222]

Polydiacetylene with R = $(CH_2)_4OSO_2C_6H_4CH_3$-*p*, obtained by the γ-radiation-induced polymerisation of the monomer (42% conversion—1 Mrad; 68% conversion—3 Mrad) dissolves at room temperature in many polar solvents (chloroform, dichloroethane, DHF, DMF, acetone, nitrobenzene, and nitromethane).[43] The yellow-orange solution has λ_{max} = 466 nm and $\varepsilon_{max} = 16.7 \times 10^3$ litre mol^{-1} cm^{-1}. The addition of a precipitant alters the colour to red with formation of a deposit. The study of PDA solutions by the light scattering and gel permeation chromatographic (GPC) methods has been shown that the macromolecules in solution have a helical conformation and that $\bar{M}_w = 7.4 \times 10^5$ and $\bar{M}_w/\bar{M}_n = 2$.[43] A broadening and shift of the MWD maximum towards higher values of $\bar{M}_n$ ($\bar{n} = 60-2000$) with increase in the degree of conversion from 2 to 10% has been observed for this PDA. Subsequently the position of the MWD curve hardly changes.[136] According to light scattering and osmometric data,[223] the shape of rigid rodlike helices, consisting of linear segments, is also characteristic of the molecules of PDA with R = $(CH_2)_2$. .OCOR′ (R′ = isopropyl, benzyl, or 1-naphthyl) in solution in $CHCl_3$, for which $\bar{M}_w = (8-13.4) \times 10^5$, $\bar{M}_n = (2.4-3.4) \times 10^5$, and $\bar{M}_w/\bar{M}_n = 3.33-3.94$.

It has been observed that soluble oligomers of hepta-2,4-diynoic acid[133] and the DA (IX) ($m = n = 4$) have the cumulene structure (II) according to infrared spectroscopic data.

The readily soluble PDA with R′ = $(CH_2)_{11}CH_3$ and $R^2 = CH_2OH$ (decalin, 100 °C) and also with $R^1 = (CH_2)_{11}CH_3$ and R^2 = COOH (nitrobenzene, DMF, HMP, 100 °C; pyridine, 20 °C) have $\lambda_{max} \cong 460$ nm in solution and $\lambda_{max} \cong 550$ nm in the single crystal, which can be explained by the altered conformation of the macromolecular skeleton.[224]

In order to investigate the conformational transitions of the polymer chains in solutions, polymers of symmetrical DA, containing in the long side substituents a large number of polar (−CO−, −NH−) and flexible (−O−, $-CH_2-$) groups have been specially synthesised.[65] The degree of interaction of the side substituents with the solvent via such groups increases and hence also the solubility of the PDA molecules. Diacetylenes with R = $(CH_2)_nOCONHCH_2COO(CH_2)_mCH_3$ are relatively inactive for $n = 2$ and are totally inactive for $n = 1$ in topochemical polymerisation. The crystals of the 3BCMU, 3ECMU, and 4ECMU monomers became coloured on heating and γ-irradiation. According to X-ray diffraction data, the specimens of poly-3BCMU, obtained with a low degree of conversion, are in the main amorphous, which has been explained[66] by the existence of only a small number of the polymer chains which determine the crystallinity of the specimen. With increase in the degree of conversion, the degree of crystallinity also increases, because an increasing number of the polmer chains become parallel to one another. The PDA of this type, obtained with degrees of conversion up to 50–92% on γ-irradiation are readily soluble in chloroform, THF, and DMF.[65] According to the GPC data (solvent—DMF), all the polymers obtained are characterised by the following features: (a) there are no intermediate oligomeric compounds, (b) the MWD is wide for all degrees of conversion, and (c) there is almost no increase in the molecular weight in the range of degrees of conversion 7–68%.[225] For example, $\bar{M}_n = 0.98 \times 10^5$, $\bar{M}_w = 4.9 \times 10^5$, and $\bar{M}_w/\bar{M}_n = 5$ for the poly-3BCMU obtained by the γ-irradiation (50 Mrad) of the monomer. The study of the viscosity of its 0.05% solutions in variable-composition solvent–precipitant mixtures (chloroform–hexane, DMF–*o*-dichlorobenzene) demonstrated the absence of an influence by the fraction of the solvent in the mixture on the viscosity of the solution, which indicated the existence of an extended conformation of the rigid polymer chains in all the solutions investigated. The extended conformation of the macromolecule is also retained on extraction of the monomer which failed to react from the partly polymerised PDA single crystal or on fusion of the single crystal.[225] Since the number of units in the polymeric 3BCMU and 4BCMU molecules is known, amounting to 10^3 and 2.4×10^3 respectively,[225–227] the length of such rigid chains was determined and was found to be ~5×10^3 and 12×10^3 Å. The same number of units in poly-4BCMU has been found by the actinometric method.[120] The electronic absorption spectra of solutions of poly-BCMU in DMF have λ_{max} = 470–475 nm and $\varepsilon \cong 17.5 \times 10^3$ litre mol^{-1} cm^{-1}.[221]

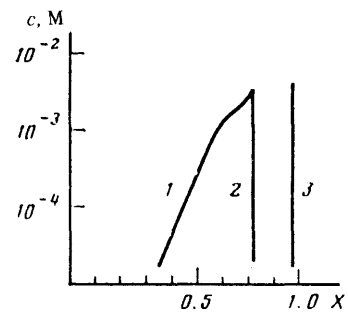


Figure 13. The phase diagram of poly-3BCMU in the chloroform–hecane system; the regions of the blue deposit (curve *1*), the blue solution (curve *2*), and the yellow solution (curve *3*) are designated as a function of the molar concentration of PDA (c) and the mole fraction of $CHCl_3$ (X).[228]

It has been observed that the addition of hexane (a precipitant) to yellow solutions of BCMU and ECMU in chloroform leads to a sharp reversible change of the colour of the solution to blue (3BCMU) or red (4BCMU). The coloured solutions are stable and do not give rise to a precipitate on standing after ultracentrifugation. An increase of the

fraction of hexane leads to the precipitation of the polymers.[105,225,227-230] The precipitation point of the deposit is strongly dependent on the polymer concentration, while the colour transition point is independent of the polymer concentration but is specific to each polymer of the series considered (Fig. 13 and Table 6).[228] Direct titration and back titration lead to different values of the $CHCl_3$ fraction (X and X') at the colour transition point. The quantity X (titration of the chloroform solution with hexane) is then always smaller than X' (titration of the blue solution with chloroform) (Table 7).[229] The solvatochromic phenomenon observed had been explained by conformational transitions of the polyconjugated PDA molecules whose optical spectrum is determined by the length of the continuous conjugation and not the chain length. In the yellow solutions the planarity of the polymer chains is perturbed by the rupture of the intermolecular hydrogen bonds, the interactions of the side substituents with the solvent ($CHCl_3$), and the rotation of the molecules about the C–C bond. The addition of a precipitant (hexane) weakens the PDA–solvent interaction and leads to a conformational transition in the macromolecules with the formation of a planar zig-zag structure of the polymer chains, fixed by hydrogen bonds, with a high effective conjugation length.[105,228-231]

Table 6. Solvatochromic and thermochromic properties of a PDA solution.[228,233,234]

PDA	K, %	X	Q, kJ mol^{-1}	T_p		
				o-dichlorobenzene	nitromethane	ethyl methyl ketone
Poly-4BCMU	92	0.55	35±2	49, 58*	52, 60	42, 47
Poly-4ECMU	75	0.65	25±2	85, 97	60, 71	72, 85
Poly-3BCMU	53	0.71	27±2	93, 102	—, 92	—
Poly-3ECMU	50	0.91	—	**	**	**

Notation: K is the degree of conversion, X the mole fraction of $CHCl_3$ at the solvatochromic transition point, Q the heat of solution, and T_p the temperature of the rupture of the hydrogen bonds of PDA in various solvents.

*The first figure denotes the dissociation of the intermolecular bonds and the second the dissociation of the intramolecular bonds.

**Poly-3ECMU dissolves only in highly polar solvents (DMF) to form a yellow solution immediately.

The effectiveness of the formation of hydrogen bonds in the 3BCMU polymers is greater than in the 4BCMU polymers owing to the difference between the lengths of the side substituents (the values of n in the side substituents).[226] Indeed construction of models taking into account the hydrogen bonds showed that the capacity of 4BCMU for polymerisation is higher, which has been reflected in the kinetics of the polymerisation of these two monomers.[105,227,228] The difference between the absorption band shifts of the 3BCMU and 4BCMU polymers in the course of conformational transitions has been accounted for by the difference between the densities of the hydrogen bond networks.[227] The strong influence of hydrogen bonds on the physicochemical processes in PDA has been demonstrated by adding small amounts of trifluoroacetic acid (acetic acid is ineffective) to the blue or red solution of poly-BGMU, which resulted in an instantaneous alteration of the colour to yellow. This colour transition is associated with the rupture of the intramolecular hydrogen bonds in the PDA network, the formation of hydrogen bonds between the added acid and the ether and urethane groups of PDA, and finally the subsequent conformational transition of the polyconjugated macromolecules.[227,228,231]

The solvatochromism of solutions of sparingly soluble (~10^{-4} mol litre^{-1} in DMF) PDA with R = $(CH_2)_nOCONHC_6H_5$ (n = 3, 4) when a precipitant is added to them can be accounted for by a similar intramolecular hydrogen bond formation process.[232]

Table 7. Solvatochromic transition points for solutions of poly-3BCMU.[229]

Dose, Mrad	K, %	Molecular weight			T_t, °C	Mole fraction of $CHCl_3$ at the colour transition points	
		$10^{-6}\overline{M}_n$	$10^{-6}\overline{M}_w$	$\overline{M}_w/\overline{M}_n$		X	X'
0.09	20.9	1.33	3.90	2.93	20	0.66	0.80
0.09	20.9	1.33	3.90	2.93	0	0.68	0.84
45	57.5	0.0802	3.18	39.7	22	0.70	0.89
45	57.5	0.0802	3.18	39.7	0	0.73	0.96

Notation: K is the degree of conversion, T_t the transition temperature, X the mole fraction obtained by titrating the yellow chloroform solution with hexane, and X' the mole fraction obtained by titrating the blue solution with chloroform.

Poly-BCMU and poly-ECMU are sparingly soluble in xylene, *o*-dichlorobenzene, ethyl methyl ketone, and certain other solvents. However, with increase of temperature, they dissolve and this is accompanied by sharp and reversible (hysteresis) colour changes. For example, the yellow solution of poly-3BCMU in *o*-dichlorobenzene (t = 106 °C) becomes blue at t < 80 °C, while the yellow solution of poly-4-BCMU (t > 68 °C) becomes red at t < 40 °C.[233] Heating PDA in a poor solvent leads to the reverse process. Thus, when red fibrillar particles of poly-4BCMU are stirred for 0.5 h at 49 °C, a red solution is formed in *o*-dichlorobenzene. Rapid heating (for less than a minute) at 58 °C gives rise to a yellow solution of PDA. Regardless of the solvent employed, the crystals of poly-4BCMU and poly-4ECMU initially form a red solution and then, on raising the temperature, a yellow solution (Table 6).[234] The heat of solution of each PDA is almost independent of the solvent.[233,234] A study of solutions and gels of these PDA by infrared spectroscopy, ^{13}C NMR, and DSC made it possible to explain the colour transitions occurring on raising the temperature by the successive dissociation of initially intermolecular and then intramolecular hydrogen bonds with formation of a non-planar conformational structure in yellow solutions at a higher temperature.[226,232-235] A decrease of temperature is accompanied by the reverse processes. The narrow temperature ranges of the thermochromic transitions indicate the cooperative character of the processes. The presence of isobestic points in the electronic spectra at 510 and 490 nm indicates the presence of a conformational equilibrium planar structure (red or blue solution or gel)–non-planar structure (yellow solution).[233]

The latest studies on poly-3(4)BCMU have shown§ that coloured solutions (blue or red) in a poor solvent are not true solutions. Thus the explanation of the colour change in the PDA solution by a conformational transition in individual rod-like conjugated macromolecules, leading to a change in the effective conjugation block is not correct and final¶.[225]

The thermochromic transition in solution has also been observed for PDA with R = $(CH_2)_4OCONHCH_2CH_3$. Its solution in DMF at 100 °C has the yellow colour characteristic of a non-planar conformation of the macrochains (λ_{max} = 470 nm), while at room temperature it has the orange colour of the planar conformation (λ_{max} = 520 nm). However, this phenomenon was not observed for the phenyl-containing DA with a similar structure [R = $(CH_2)_m$. .$OCONHC_6H_5$, where m = 3, 4] even in the presence of a precipitant.[232]

It has been reported that, on treatment with ultrasound in water, DA with R = $(CH_2)_8CH_2OP(O)(OH)_2$ dissolves and polymerises (irradiation with ultraviolet light) with formation of a dark-blue thermochromic solution.[236] However, in this case a true solution is apparently not formed, since the topochemical polymerisation of DA cannot take place in it.

A visible conformational transition has been observed in aqueous solutions of PDA with the symmetrical substituents $(CH_2)_nCOO^-K^+$ (n = 2, 3) and $(CH_2)_3OCONHCH_2COO^-K^+$.[67,68] The solution of the first polymer has a yellow colour at pH ≥ 7. The maximum in its absorption spectrum shifts from 462 to 535 nm when the pH is reduced from 9.5 to 3,, while at low pH (after the addition of HCl) an absorption band with λ_{max} = 575 nm appears in addition. The change in the colour of the solution to red or purple takes place because the planar conformation of the macrochain, which obtains for polymers with the COO^-K^+ groups at pH < 7, is perturbed with increase of the pH by virtue of the formation of the ionic groups COO^-, between which there is a powerful electrostatic repulsion. At pH < 2 a blue-black polymer is precipitated. The introduction of an electrolyte (LiCl, NaCl, KCl) into the solution, leading to a suppression of the dissociation of the ionogenic COO^-K^+ groups and the subsequent decrease of the repulsion between then, has a lesser influence on the conformation. It is of interest that, when the concentration of the electrolyte was altered, the existence of an isosbestic point was noted but the latter vanished when the pH of the medium was altered.[68] The character of the influence of the pH and the electrolyte on solutions of two other polymers is analogous and the difference observed in the shift of the maxima of the absorption spectra of the solutions has been explained by the different distances of the terminal COO^-K^+ groups from the main chain.[68] The salt-like PDA of this class can be synthesised only via the corresponding polymeric acids with subsequent formation of their salts in

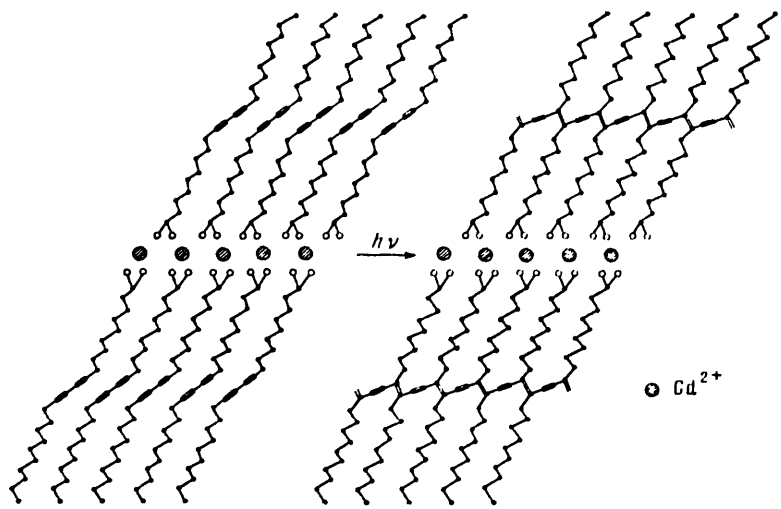


Figure 14. The structure of the cadmium salt of poly-DA in the monolayer.[192]

§G.Wenz, M.A.Müller, M.Schmidt, and G.Wegner, Macromolecules, 1984, **17**, 837; M.A.Müller, M.Schmidt, and G.Wegner, Macromol.Chem.Rapid.Comm., 1984, **5**, 83.

¶K.C.Lim, L.A.Fincher, and A.Heeger, Phys.Rev.Letters, 1983, **50**, 1934.

the presence of alkalis. The monomeric potassium and sodium salts of the DA acids are incapable of topochemical polymerisation.[67]

V. MONOMOLECULAR AND POLYMOLECULAR LAYERS BASED ON DIACETYLENES

The principles of the topochemical polymerisation of diacetylenes in single crystals examined earlier are also valid in the solid-phase polymerisation of DA packed into thin layers. Studies in this field have been vigorously prosecuted[237] in connection with the extensive possibilities for the practical application of such layers.

Monomeric monolayers were first obtained using tricosa-10,12-diynoic acid $C_{10}H_{21}C\equiv C-C\equiv C(CH_2)_8COOH$.[192] It was noted that, from the standpoint of the solubility of the layers, the cadmium salt of this acid, forming in the mono-layer a polymer whose structure is illustrated in Fig.14, is more suitable as regards the stability of the layers. The method of preparation of the monomolecular and polymolecular layers has been described†.[238] the monomolecular or polymolecular layers of the monomers satisfied the criteria for topochemical polymerisation and polymerised under ultraviolet irradiation via 1,4-addition without breakdown of the layer structure and with formation of ultrathin films, which are stable under laboratory storage conditions (oxygen, light, etc.).[192,239] The polymerisation of the macromolecular and polymolecular layers, like that of single crystals, can proceed thermally (below the melting point) and under the influence of high-energy radiation.[224]

Subsequently layers based on a whole series of asymmetrically substituted DA (XIII) were obtained similarly and then investigated:

$$CH_3(CH_2)_m-C\equiv C-C\equiv C-(CH_2)_nCOOH\ ;$$
(XIII)

m = 4, 7, 9, 11, 13, or 15, n = 8;[190,191,240,241] m = 2–15, n = 0, 2, 3, or 8:[242] DA with $R^1 = (CH_2)_{11}CH_2$ and R^2 = CH_2OH or COOH.[224] The monomers synthesised exhibit different capacities for the formation of monolayers and for polymerisation in the latter (Table 8).[216,239] It has been observed that the polymerisation of DA in monolayers, initiated by ultraviolet radiation, must be carried out in an inert atmosphere, since the reaction in oxygen leads to the formation of ozone under the influence of which the polymer chains are ruptured.[190,243] As a result of this, the side chains replace the main chains and thereby expand the monolayer, disrupting it.[190] It has been noted that the stability of layers increases with increase in the m/n ratio in compound (XIII). The layers are stronger when the aqueous phase on which the film is formed contains the Cd^{2+}, Ba^{2+}, Ca^{2+}, Fe^{3+}, or Al^{3+} ions.[242]

Polymerisation results in contraction, the extent of which makes it possible to infer the degree of conversion. The change in the degree of conversion was compared with the change in the optical density in the electronic spectra and with the position of the maximum in the absorption spectra.[190,191,240] It has been shown[190,191] that diacetylenes having the general formula (XIII) (m = 11, 13, 15; n = 8) polymerise rapidly in a monolayer at 20 °C (ultraviolet radiation). For m = 9, the polymerisation proceeds only at 2 °C, while acids with still shorter chains (m = 4.7) do not polymerise under such conditions. With increase in the pH of the aqueous phase, the rate of polymerisation increases when the lithium, sodium, and potassium salts of the acid are employed. The use of the Be^{2+}, Cd^{2+}, and Ba^{2+} ions[190,191] and Ca^{2+} and Mg^{2+} ions[190,243] perturbs the packing of the monomer molecules in the layer and suppresses the polymerisation process at high pH. With decrease of pH to below 6 (by adding HCl), the polymerisation proceeds to completion also in the presence of bivalent ions.[191]

†L.M.Blinov, Uspekhi Khim., 1983, **52**, 1263.

Table 8. The capacity of DA acids for the formation of monomolecular and polymolecular layers and for polymerisation in the latter.[239]

DA	M.p., °C	Capacity for formation of monomolecular layers		Formation of polymolecular layers	Photopolymerisation at $\lambda < 300$ nm[1]	
		on water	on 10^{-3} M $CdCl_2$ soln		in the crystal	in polymolecular layers
n-C_9H_{19}—C≡C—C≡C—$(CH_2)_8$—COOH	48	yes	yes	—	++	—
n-$C_{10}H_{21}$—C≡C—C≡C—$(CH_2)_8$—COOH	57	yes	yes	yes	++	+
n-$C_{12}H_{25}$—C≡C—C≡C—$(CH_2)_8$—COOH	61	yes	yes	yes	++	+
n-$C_{14}H_{29}$—C≡C—C≡C—$(CH_2)_8$—COOH	46/59[2]	yes	yes	yes	++	+
n-$C_{12}H_{25}$—C≡C—C≡C—$(CH_2)_8$—COOH	57	yes	yes	no	++, +[3]	—
n-$C_{16}H_{33}$—C≡C—C≡C—$(CH_2)_2$—COOH	93	yes	yes	yes	++	—
n-$C_{16}H_{33}$—C≡C—C≡C—COOH	75	yes	yes	yes	+++	+
n-$C_{12}H_{25}$—C≡C—C≡C—COOH	58	no	no	no	++	—
n-$C_{10}H_{21}$—C≡C—C≡C—$(CH_2)_9$—OH	49	yes	yes	no	+	—

Remarks: [1]+++ = dark-blue after less than 10 s; ++ = dark-blue after 10–30 s; + = dark-red after more than 2 min; − = no reaction. [2]Phase transition at 46 °C. [3]There are two modifications with different reactivities.

The study of the acid $CH_3(CH_2)_{17}C\equiv C-C\equiv C-COOH$ and of a series of its salts (NH_4^+, Ag^+, Na^+, Cd^{2+}, Cu^{2+}, Hg^{2+}, and Mn^{2+}) with the aid of optical and infrared spectroscopy and EPR showed that the acid itself and its silver and ammonium salts polymerise in the polymolecular layers (the PDA have respectively λ_{max} = 670 and 635 nm), the topochemical polymerisation of the cadmium, sodium, and manganese salts does not occur, while the polymerisation of the copper and mercury salts is accompanied by the decarboxylation of the DA.[244,245] The non-linear optical susceptibility of the blue polymeric ammonium salt is the same as that of the PDA with a $-(C\equiv C)_2-$ group in the centre of the aliphatic chain.[245]

In the polymolecular layers the alkyl side substituents of the monomers (XIII) (m = 2–15, n = 0, 2, 3, 8) are inclined at an angle of 48–63° relative to the support in each monolayer. During polymerisation, the substituents become almost perpendicular to the surface of the support, which results in the observation of the phase transition accompanied by a hypsochromic shift of the maximum in the absorption spectrum.[242]

According to X-ray diffraction and electron microscope data, the PDA chains are extended in the monolayer parallel to the support, while the layers have the crystalline domain structure and are made up of a mosaic of blocks or crystallites. The average size of the domain in which there is a homogeneous orientation of the main PDA chains depends on the conditions of the preparation of the layers and is of the order of several μm.[190,200,239,246,247] In a two-layer and multilayer membrane both monolayers retain the individual morphology of the crystallites.[248,249] Various modifications of the monomeric and blue polymeric layers as well as the transitions between these modifications have been investigated by electron microscopy (Fig.15).[250]

A crystalline dichroic fibre with a thickness of the order of several micrometers has been obtained by withdrawing from the surface of water a PDA acid monolayer. In these fibres the long lateral paraffinic chains, deviating from the polymer units, are oriented at right angles to the fibre axis and form crystallites which are packed at random across the fibre.[190] The tensile stress in the PDA fibres is comparable to that for the usual non-oriented polymers and the modulus of extension is high, due to the high degree of crystallinity. An increase in the size of the crystallites is then accompanied by an increase of the modulus.[251]

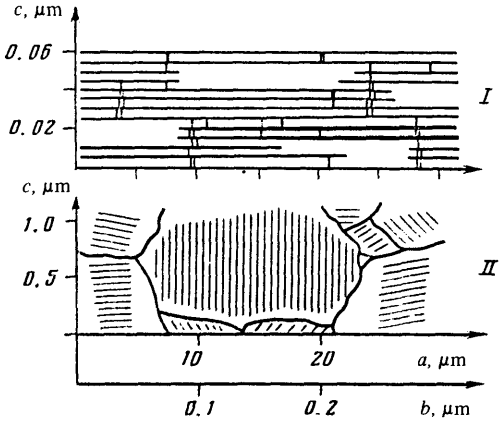


Figure 15. A model of the polymolecular layers based on $CH_3(CH_2)_nC{\equiv}C{-}C{\equiv}C(CH_2)_8COOH$ at right angles (I) and parallel (II) to the specimen; *A*) and *B*) DA; *A'*) and *B'*) PDA; *A*) and *A'*) the low-temperature phase; *B*) and *B'*) the high-temperature phase ($t > 60$ °C). The dimensions of the low-temperature (*A* and *A'*) phase (*a*) and the high-temperature (*B* and *B'*) phase (*b*) are indicated along the horizontal axes. Sections with parallel cross-hatching represent identically oriented planes.[250]

Polymolecular layers have been used to determine the quantum yield ϕ of the photochemical polymerisation of DA. The specimens used were films deposited on quartz plates and consisting of 32 monolayers of the diynoic acids (XIII) ($m = 9$, 11, 13; $n = 8$). The initial value of ϕ (the number of DA molecules which have reacted for each absorbed light quantum) is 10–14, so the polymerisation has the character of a chain reaction. With increased degree of conversion, ϕ falls rapidly for all the monomers investigated.[252]

On the basis of the results of the study of the processes involving the photochemical topochemical polymerisation of diacetylenic acids in polymolecular layers, sensitised by the surface-active cyanine,[246,253] acrydine, and anthraquinone[255] dyes, models have been proposed for the sensitised photochemical polymerisation of DA.[246,253–255] The quantum yield ϕ depends on the amount of sensitiser, depends only slightly on temperature, and is independent of the light intensity.[246] The photochemical topochemical polymerisation is initiated solely by ultraviolet light with $\lambda \leq 313$ nm. After the formation of small amounts of PDA, the polymerisation occurred in the range $400 < \lambda < 500$ nm.[256] The observed effect of the self-sensitisation of the photochemical topochemical polymerisation of the polymolecular layers has been explained by the generation of the PDA chains of highly mobile charge carriers, which activate the centre capable of polymerisation present at the end of the chain, ensuring further chain propagation.[256]

For the polymerised polymolecular layers of the cadmium salts of the DA acid $CH_3(CH_2)_{11}{-}C{\equiv}C{-}C{\equiv}C{-}(CH_2)_8COOH$, a thermochromic transition has been observed (Fig.16).[247]

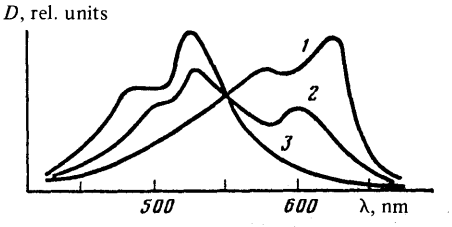


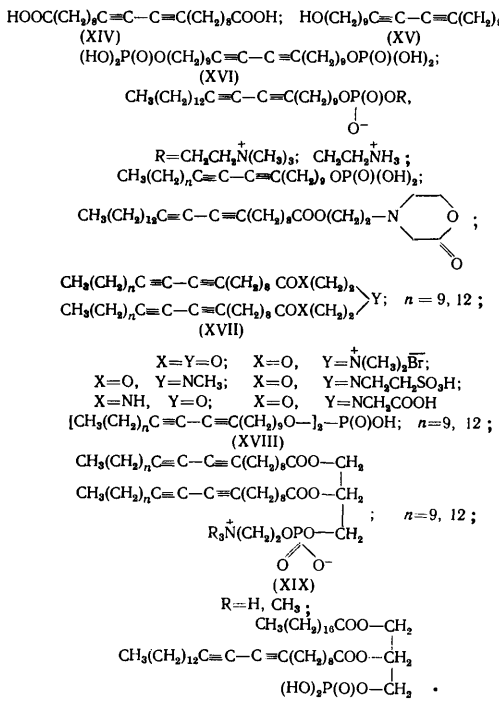
Figure 16. The thermochromic transition in polymolecular layers of the cadmium salts of the PDA acid $CH_3(CH_2)_{11}{-}C{\equiv}C{-}C{\equiv}C{-}(CH_2)_8COOH$; temperature (°C): 1) 23; 2) 52; 3) 91.[247]

Apart from the monomolecular and polymolecular layers based on individual acids and their salts, polymolecular layers made up of mixtures of different acids and their cadmium salts have been investigated. An increase in the stability of mixed polymolecular layers based on the cadium salts of pentacosa-10,12-diynoic and arachidic acids (the latter is inactive in topochemical polymerisation) has been observed relative to the stability of polymolecular layers of the pure diynoic acid. In mixed layers the components form individual domains whose structure resembles that of the monolayers of the corresponding pure components. At a low concentration pentacosa-10,12-diynoic acid forms domains whose size is <0.1 μm, while the second component forms large domains whose size extends to several μm. It is of interest that, with increase of the concentration of the diynoic acid, the dimensions of its domains also increase but the degree of conversion nevertheless falls.[257] Polymolecular layers of the cadmium salts of tricosa-10,12-diynoic and tricosa-4,6-diynoic (less reactive) acids also separate into phases, but, in contrast to the previous pair of acids, another picture is observed: when the concentration of one of the components exceeds 50%, the polymolecular layer consists of a mixture of domains of this pure component and of domains of a crystalline complex of the acid components in 1 : 1 proportions.[257]

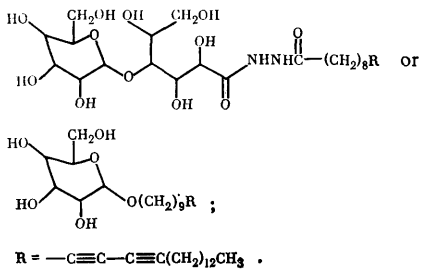
It has been suggested that the thickness of the polymolecular layers based on DA acids could be determined from the standard bond lengths and valence angles. However, the lack of validity of this approach owing to the ambiguity in the conformations of the individual CH_2 groups of the paraffinic moieties of the diacetylenic acids has been demonstrated.[250]

The chiral DA–$CH_3(CH_2)_{11}{-}C{\equiv}C{-}C{\equiv}C{-}(CH_2)_8CONH{-}\overset{*}{C}H(CH_3){-}C_6H_5$ polymerises rapidly in polymolecular layers on irradiation with ultraviolet light and X-rays. Even under the influence of scattered laboratory light, the topochemical polymerisation of layers of this monomer at the air/water interface takes place in seconds.[198]

The development of the principles governing the preparation of strong monomolecular and polymolecular layers based on diacetylenic acids and their salts and the study of the topochemical polymerisation of diacetylenes made it possible to obtain a whole series of polymeric membranes and DA-based liposomes modelling the natural lipids and certain functional compounds:[258-264]



The polymerisation of the diacetylenic phosphorylcholine (XIX) (R = CH_3, n = 12) initiated by ultraviolet light (argon) in a monolayer leads to the formation of a polymeric phospholipid coloured red and exhibiting optical activity.[265-267] The topochemical polymerisation of phospholipids containing one of two residues of tricosa-10,12-diynoic acid has been investigated on the basis of the contraction of the layers and various types of structures corresponding to phospholipid polymers have been examined taking into account the intra- and intermolecular cross-links involving both one and two acyl groups containing the C≡C–C≡C bond.[266,267] Spherical multilayer lipsomes 4000 Å in diameter have been obtained by hydrolysing suspensions of diacetylenic phospholipids.[266] Structures modelling liposomes have been obtained also by treating the DA (XVI) with ultrasound in water in the presence of cholesterol with subsequent ultraviolet irradiation.[236] On the other hand, on treatment with ultrasound, the symmetrical DA (XIV) and (XV) form crystalline suspensions in water, which do not model liposomes.[236]



The phototopochemical polymerisations of the lipid DA (XVII) [n = 9, X = O, Y = $\overset{+}{N}(CH_3)_2Cl^-$], (XVIII) ($n$ = 9), and (XIX) (n = 9, R = CH_3) have been compared. It has been shown that the capacity of compound (XIX) for polymerisation is appreciably lower than that of the other two DA. The quantum yield of the phototopochemical polymerisation of compound (XVII) is ~6500 times higher than for compound (XIX).[268]

Naturally non-polymerising lipids {distearyl- and dioleylphosphatidylcholine and cholesterol combined with lipids having DA groups in the chain, for example (XIX) (n = 9, R = CH_3) and (XVII) (n = 9, X = O, Y = $\overset{+}{N}(CH_3)_2Cl^-$; n = 12, X = O, Y = $\overset{+}{N}(CH_3)_2Br^-$; n = 12, X = O, Y = $-(CH_2)_2O(CH_2)_2O(CH_2)_2O(CH_2)_2-$)} form mixed monomolecular and bimolecular layers, consisting of domains, or homogeneous membranes, depending on the type of the monomeric and natural lipid.[269-272] It has been observed that, when systems of this kind are acted upon by the enzyme phospholipase A_2, only the natural lipids are hydrolysed and in layers with separated phases the rate of cleavage is the same as in layers comprising one of the natural lipids; the rate is much lower in homogeneous layers.[270]

The biological models of two-layer lipid membranes synthesised in this way have been investigated by electronic spectroscopy for chemical analysis (ESCA). The presence on the surface of the layers of the elements (P, N, Br, and C) which enter into the composition of the functional group has been demonstrated. The angle of wetting by water θ, which decreases when the monolayers with a hydrophobic surface are kept in air, has been determined. It has been observed that for hydrophilic polymers the nature of the functional groups has less influence on θ for the monolayer than in the case of a hydrophobic polymer.[273]

The preparation of thin films based on PDA with the aid of other methods without employing the principles governing the formation of Langmuir–Blodgett monolayers has been described. These films also demonstrate the specific character of the properties of the polymers.

Thus a thermochromic colour change (at 455 K) from green to yellow has been observed in amorphous films of poly-3BCMU obtained by precipitation from dilute chloroform solutions of PDA with hexane and subsequent drying. The reverse colour change occurs at 435 K. It has been shown by DSC and infrared spectroscopy that the thermochromism is associated with a one-dimensional order ↔ disorder transition, which is determined by the disruption or formation of hydrogen bonds along the polydiacetylene chain containing the C(O)O and NH groups.[274] This explanation of the phenomenon is similar to that given when the thermochromism of single crystals of the same nature was considered.[65]

Thin PDA films with R = $(CH_2)_nOCONHC_6H_5$ (n = 1, 4) and R = CH_2OH have been obtained by an epitaxial mechanism on the surfaces of alkali metal halide single crystals. It has been shown by electron microscopy and electron diffraction that the films consist of highly oriented lamellar single crystals extended in the direction of their maximum dimension along the [110] crystallographic direction on the support.[275]

VI. MECHANICAL PROPERTIES OF POLYDIACETYLENES

A negative coefficient of thermal expansion α has been observed for a series of PDA single crystals along the direction of the polymer chains. Thus $\alpha = -(1.686 \pm 0.039) \times 10^{-5} - (1.35 \pm 0.18) \times 10^{-7}t$ (t in deg C) for a freshly prepared poly-HDDU specimen[53,276] in the temperature range

$t = -50-100$ °C, diminishing by an order of magnitude after evaporation of the dioxan occluded in the single crystal. The coefficient of thermal expansion of the same polymer in the direction of the chain has been determined in another study[277] as -2.0×10^{-5} K^{-1}. For poly-DCHD, $\alpha = (-2.38 \pm 0.07) \times 10^{-5}$ K^{-1}.[70] The coefficient α for poly-TS is negative below 70 K and positive above this temperature, the change in the coefficient within the range of hydrostatic pressures 0–3.43 kbar not exceeding the error of measurement.[278]

Negative values of α had been observed earlier for certain partly crystalline polymers, for example, polyethylene,[279] only with the aid of X-ray studies, since the negative value of α characteristic of the crystalline phase, is masked by the significantly more positive α for the amorphous component. Explanations of the anomalous behaviour of the coefficient α, involving the use of the principle that the amplitude of the torsional movement (torsional vibration) of the chain increases with temperature,[279] have been put forward.[53,277]

It has been concluded[276] that the sign of the coefficient α is not determined by the change in the delocalisation of π electrons arising owing to the thermal conformational fluctuations or the reversible formation of defects, since the theoretically possible calculated contribution to the coefficient should be much less than the value actually observed. Subsequently[278] the unusual behaviour of the coefficient α was analysed in terms of an equation including the Grueneisen parameter and it was postulated that this behaviour is caused by the characteristic properties of the PDA chain.

The positive value of the coefficient observed solely for the polymer based on compound (IX) ($m = n = 4$) in the temperature range $-50-40$ °C ($\alpha = 4.46 \times 10^{-6}$ K^{-1}) has been attributed[179] to the presence of $-(C\equiv C)_2-$ groups which failed to react, which leads to disordering of the chains and the conversion of the polymer into an amorphous form.

The mechanical properties of traditional polymers are determined to a large extent by the presence in them of structural and phase defects. For very perfect PDA crystals made up of extended macrochains, there is a possibility of particularly high strength properties of the polymer molecules within the macrovolume of the specimen with the simultaneous manifestation of a pronounced anisotropy: the modulus in the direction of chains is much higher than that for the direction at right angles to the chains.[280]

The dynamic and static moduli of extension of the crystalline fibres of poly-HDDU, obtained in the region of elastic deformations, are virtually identical (~4.5×10^4 N mm^{-2}).[52] The observed deviation from Hooke's law (the decrease of the modulus by ~3 and 6% on 3 and 4% deformation respectively) is analogous to the behaviour of other filamental crystals, for example, those of iron, quartz, etc. The tensile strength, reaching 1.7×10^3 N mm^{-2}, usually increases with decrease of the length of the fibre and is approximately proportional to the reciprocal of the fibre diameter. The latter factors can be accounted for by the existence on the surface of the fibre (or in its vicinity) of a small number of defects, which control the disruption process. Indeed photographs obtained with the aid of a scanning electron microscope demonstrated the formation of a crack on the surface of the crystal after the tensile strength has been exceeded, the crack spreading initially to a certain depth and then along the fibre. As a result of this, the crystal is partly cleaved and there is an irreversible slip of its two components relative to one another.[52]

The tensile strength of PDA with R = $CH_2OCONHC_2H_5$ (diameter 10–100 μm, length up to 5 cm) is also proportional to the reciprocal of the fibre diameter. The tensile strength, which increases with increase in the degree of conversion, amounted to $(0.6-1.4) \times 10^3$ N mm^{-2} for a relative elongation of 12–20%, but in a number of instances it reached 6.2×10^4 N mm^{-2}. Creep was not observed in the fibres.[281]

Poly-TS specimens increase in length by 4% before they are ruptured: the corresponding tensile strength is 2.0×10^3 N mm^{-2}.[282] The degree of conversion in the thermal polymerisation of TS (60 °C) has been followed by measuring the frequencies of phonons with wave vectors parallel to the *a*, *b*, and *c* axes of the crystal. It has been shown that the density varies from 1.404 to 1.483 g cm^{-2}, while the modulus of elasticity increases in the direction of the chains from 0.97×10^4 to 4.38×10^4 N mm^{-2} on passing from the monomer to the polymer.[58]

It has been observed that the Raman spectra of the deformed and undeformed regions of poly-TS are identical[280,283] and the *b* axis of the unit cell, which is the direction of the main PDA chain, should therefore remain unchanged. A transition from the monoclinic to the triclinic unit cell has been observed in the deformed regions of poly-TS.[280] Under these conditions, the *a* axis is unchanged, while the *b* axis and the angle β are altered, which diminishes the volume of the cell by ~7% and leads to closer packing of the polymer chains in the deformed regions.[36] The slip planes in the deformation of poly-TS crystals have been determined.[36,52]

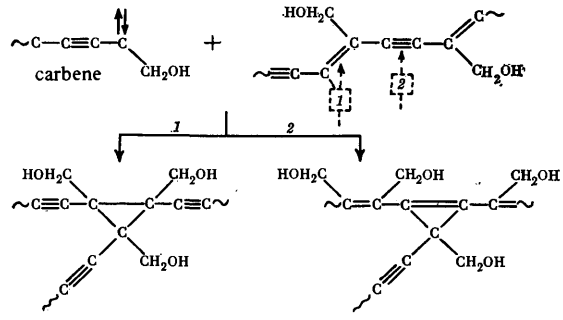
A ladder polymer based on compound (IX) ($m = n = 4$)[179,208] has a low modulus (5.5×10^3 N mm^{-2}) and tensile strength (2.2×10^2 N mm^{-2} (despite the existence of a dense cross-linked network. The reason for this is the disorder in the chains owing to the presence of $-(C\equiv C)_2-$ groups which have reacted incompletely (see Section III).[179] The tensile strength of DCHD is 0.6×10^3 N mm^{-2}.[70]

The morphology and mechanical properties of a fibre obtained from a polymerised DA layer have been investigated[271] (see Section V).

The high mechnical strength of many single-crystal PDA fibres enabled Young and Galiotis[284] to suggest that fibres of this type be used in thermoplastic and thermally hardening composite materials with high strengths and rigidities. A comparative study with the aid of resonance Raman spectroscopy (Kr laser, $\lambda = 676$ nm) of poly-DCHD fibres and fibre joints overed by an epoxy-resin (hardened with an amine) showed that the strength of the bond between the fibres and the epoxy-resin is fairly high and the tensile strength at the joint is comparable to that of a whole fibre.[285]

VII. CHEMICAL PROPERTIES OF POLYDIACETYLENES

According to mass-spectrometric data and elemental analysis, the CH_2OH side groups in the HD polymers obtained in air or in argon exhibit a high chemical stability in the course of polymerisation.[30] However, in the solid-phase polymerisation of HD crystals containing occluded oxygen, the reactive terminal carbene radicals, which propagate the polymerisation reaction, may be oxidised with formation of the ~=C(CH_2OH)–C≡C–C(CH_2OH)=O end groups. The polymerisation of HD in argon leads to a high conversion (>20%) in intermolecular interactions between the terminal carbene radicals and the multiple bonds in the polymer chains, which results in cross-linking of the polymer formed[30] in accordance with the scheme



--[ ]--► possible direction of attack by the carbene and the corresponding reaction products.

A low chemical stability in thermal polymerisation has been observed for the $R-(C\equiv C)_3-R$ polymers ($R = CH_2OH$ or $CH_2OSO_2C_6H_4CH_3$-*p*) (Table 5).[193]

The thermal stabilities of various types of PDA have been investigated. It has been observed that, despite the polyconjugated main chain, the crystalline PDA do not possess a high thermal stability owing to the presence in the macromolecules of side substituents which are unstable at a high temperature. Their thermal decomposition begins as a rule at a temperature not exceeding 200–215 °C. For example, the PDA obtained by the thermal polymerisation of TS at 60 °C would not decompose on rapid heating to 210 °C; prolonged heating induces decomposition at a much lower temperature (110 °C). The thermal decomposition of poly-TS specimens obtained at 70° and 80 °C takes place immediately after the attainment of 110 °C.[36] Mass-spectrometric studies of the molecular structure of poly-TS as well as investigation of its degradation process suggested a mechanism for the low-temperature decomposition.[40] Gas-chromatographic and mass-spectrometric studies of the products of the pyrolysis of this polymer at 400–1000 °C have shown that the main pyrolysis products are triacetylene and toluene-*p*-sulphonic acid.[40]

The poly-BPG, whose polyconjugated main chain is doubled by the chain of the side substituent coiled around it, has a higher thermal stability. The polymer loses 2 wt.% at 350 °C, 13 wt.% at 400 °C, 30 wt.% at 450 °C, and 39 wt.% at 500 °C.[103] A cyclo-ladder polymer based on compound (IX) ($m = n = 4$), possessing a dense cross-linked network, has been synthesised.[179] However, an improvement in thermal stability was not achieved primarily because of additional weight loss due to the evolution at 150 °C of the solvent cocrystallised with the initial monomer. Apart from the weight loss mentioned above at 150 °C (9 wt.%), the thermogravimetric curve shows a sharp weight loss beginning at 400 °C and reaching a maximum (48 wt.%) at 470 °C.[179]

Poly-DCHD exhibits a higher thermal stability, probably owing to the aromatic carbazolyl nuclei, being stable to 300 °C and losing 6.5 wt.% at 400 °C. However, exothermic decomposition, leading to a weight loss of 62% at 475 °C, begins between 400° and 450 °C.[70]

As in the case of polyalkynes, obtained by liquid-phase polymerisation, the polyhexa-2,4-diyne synthesised by topochemical polymerisation is vigorously oxidised by oxygen.[24] Accoring to Chance et al.,[286] the hypsochromic shift in the optical spectrum of a solution of poly-3BCMU arises partly owing to chemical defects which perturb the conjugation and appear as a result of the slow (in the course of months) oxidation of the PDA chains.

In addition, like other polyacetylenes having multiple bonds within the chain, the PDA can combine with ozone. For example, it has been observed that ultraviolet radiation causes the disruption of PDA monolayers[190,243] and decolorisation of PDA solutions[287] owing to the interaction of the main polyconjugated chains of the polymers with the ozone formed and subsequent decomposition of the ozonides.

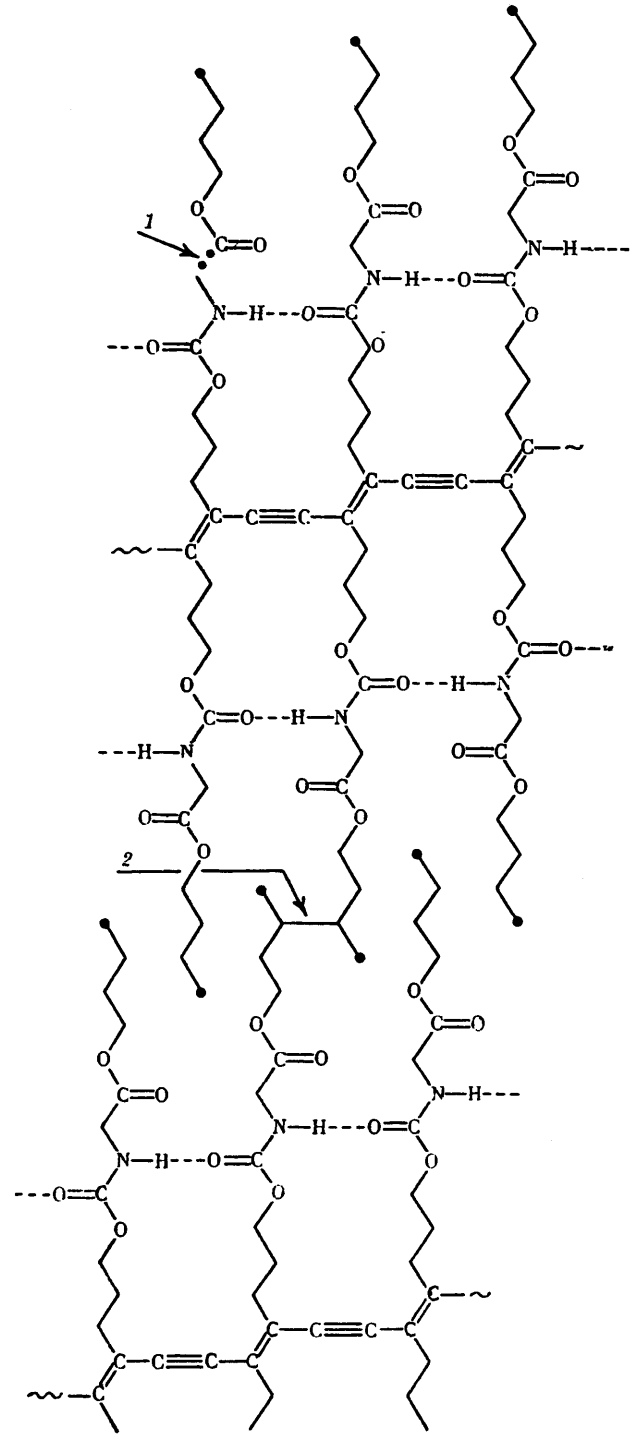


Figure 17. Schematic illustration of the decomposition of poly-3BCMU under the influence of γ-radiation: 1) disruption; 2) cross-linking.[290]

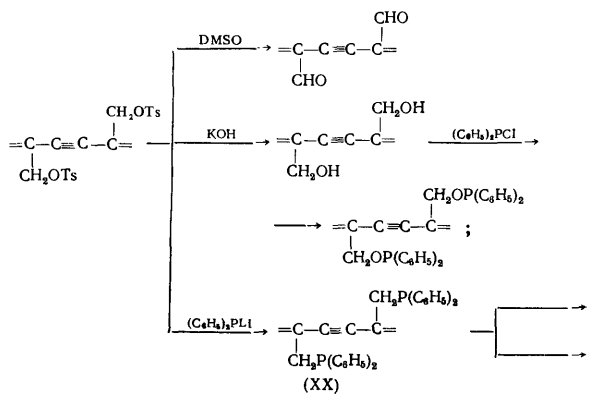
PDA washed free of monomers,[193] PDA double layers,[288] and a TS single crystal, subsequently polymerised via a topochemical polymerisation mechanism,[289] have been doped with iodine. The conductivity of the specimens then increases by several orders of magnitude but neither the mechanism of the doping process nor the structure of the products of the interaction of PDA with iodine have been studied in detail.

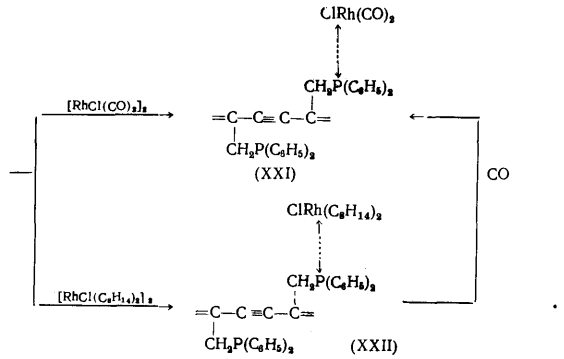
Investigation of the radiation stability of poly-3BCMU (^{60}Co γ-radiation, 20 °C, vacuum) showed that crystalline PDA remains soluble after irradiation with a dose of 50 Mrad. In amorphous PDA, obtained by dissolving and precipitating crystalline PDA, the gel fraction is formed at 3 Mrad, while for a dose of 200 Mrad the polymer loses its solubility completely.[290] It has been noted that the highly conjugated main chains do not undergo cross linking, while irradiation leads to the degradation of the side chains and their cross linking by intermolecular bonds (Fig.17). The marked decrease of $\bar{M}_n$ and the widening of the MWD with increase in the degree of conversion from 20.9 to 57.7% probably take place as a result of degradation in the course of polymerisation (Table 7).[229]

Using the chemical structure of the side substituents, PDA has been modified. Charge-transfer complexes between electron acceptors and the monomeric DA containing the anthryl or carbazolyl groups have been obtained.[69] However, it has been shown[64] that the monomeric charge-transfer complexes based on 1,6-bis(3-pyrenyloxy)hexa-2,4-diyne and electron acceptors (tetracyanoquinodimethane, tetracyanoethylene, trinitrofluorenone, etc.) do not polymerise in the solid phase. Nor are charge transfer complexes formed on treating a suspension of PDA in CH_2Cl_2 with a solution of tetracyanoquinodimethane. Only on mixing solutions of a pyrene-containing PDA and acceptors, diluted with HMP, are intensely coloured 1:1 or 1:2 complexes (depending on the type of acceptors) precipitated.[64] The equilibrium constants for the formation of the charge-transfer complexes investigated are higher than for the model charge-transfer complexes with the corresponding monofunctional compounds.

The presence of labile toluene-*p*-sulphonyl groups made it possible to carry out reactions between poly-TS and $LiP(C_6H_5)_2$ with formation of a fully phosphinated dark-brown amorphous polymer (XX) having $CH_2P(C_6H_5)_2$ side groups.[291, 292] The photomicrographs obtained with the aid of a scanning electron microscope showed a loose surface of the specimen with its area not quite so large as that of silica gel. The toluene-*p*-sulphonyloxymethyl groups have been replaced via polymer-analogue reactions by CHO, CH_2OH, and $CH_2OP(C_6H_5)_2$ groups.[292]

The study of the EPR spectra of a dry specimen of poly-TS with an attached spin label as well as specimens wetted with benzene and CCl_4 did not reveal a difference between the shapes of the spectra obtained.





Thus, in the given instance the nature of the solvent did not influence the behaviour of other molecules attached to the polymer chains.[277] The polymeric complexes $RhCl(CO)_2R'$ (XXI) and $RhCl(C_8H_{14})_2R'$ (XXII) (R' is one phosphine group in PDA)[291] have been obtained respectively by the reaction of compound (XX) with $[RhCl(CO)_2]_2$ and $[RhCl(C_8H_{14})_2]_2$ (C_8H_{14} is cyclo-octene).[291] In the presence of the complex (XXI) mono-olefins are hydrogenated by cyclohexa-1,3-diene is relatively inactive. In the presence of the complex (XXII) cyclohexa-1,3-diene is hydrogenated more rapidly to acrylonitrile than are α-olefins. Benzene is also hydrogenated at a measurable rate at atmospheric pressure. On the other hand, the "monomeric" complex $RhCl[P(C_6H_5)_3]_3$ does not catalyse the hydrogenation of conjugated olefins at atmospheric pressure. The high reactivity of the phosphinated polymeric complex is apparently associated with the increased rigidity of the polymer chains, which ensures the stabilisation of two coordination sites and prevents the formation of the chelate. Thus the possibility arises of activating both hydrogen atoms and the conjugated olefin.[291]

VIII. POLYMERISATION OF LINEAR COMPOUNDS WITH SEPARATED $-C\equiv C-C\equiv C-$ GROUPS

Linear DA of the types

$$R-C\equiv C-C\equiv C-(CH_2)_2-C\equiv C-C\equiv C-R,$$
$$R-C\equiv C-C\equiv C-(CH_2)_2-C\equiv C-C\equiv C-(CH_2)_2-C\equiv C-C\equiv C-R,$$
$$R-C\equiv C-C\equiv C-(CH_2)_2-C\equiv C-C\equiv C-C\equiv C-C\equiv C-(CH_2)_2-C\equiv C-C\equiv C-R,$$
$$R=CH_2OSO_2C_6H_4CH_3\text{-}p,\ CH_2OCONHR'(R'=CH_3,\ C_2H_5,\ C_6H_5),$$

have been proposed as temperature–time indicators.[219–293]

At 100–200 °C or under the influence of ultraviolet light, the crystalline $H_3C-C\equiv C-C\equiv C-Hg-C\equiv C-C\equiv C-C\equiv C-CH_3$ polymerises up to 100% conversion (the yield has been determined gravimetrically) with formation of violet, blue, and even red-brown insoluble crystals. The S-shaped conversion curves show an induction period, as in the case of the solid-phase polymerisation of TS. The authors[294] believe that this involves the formation reaction of a ladder polymer (Fig.18).

The presence of the $C\equiv C-C\equiv C$ groups in the long polymer chains does not rule out the possibility of the reaction involving the 1,4-cleavage of the diacetylenic groups in such chains via the mechanism described above for low-molecular-weight DA. Indeed, the oxidative condensation of nona-1,7-diyne[176,295] and dodeca-1,11-diyne[176,177,296] yielded the corresponding crystalline macromers containing reactive groups in the chain.

$$HC\equiv C[(CH_2)_mC\equiv C-C\equiv C]_n(CH_2)_mC\equiv CH;$$
$$m=5,\ 8.$$

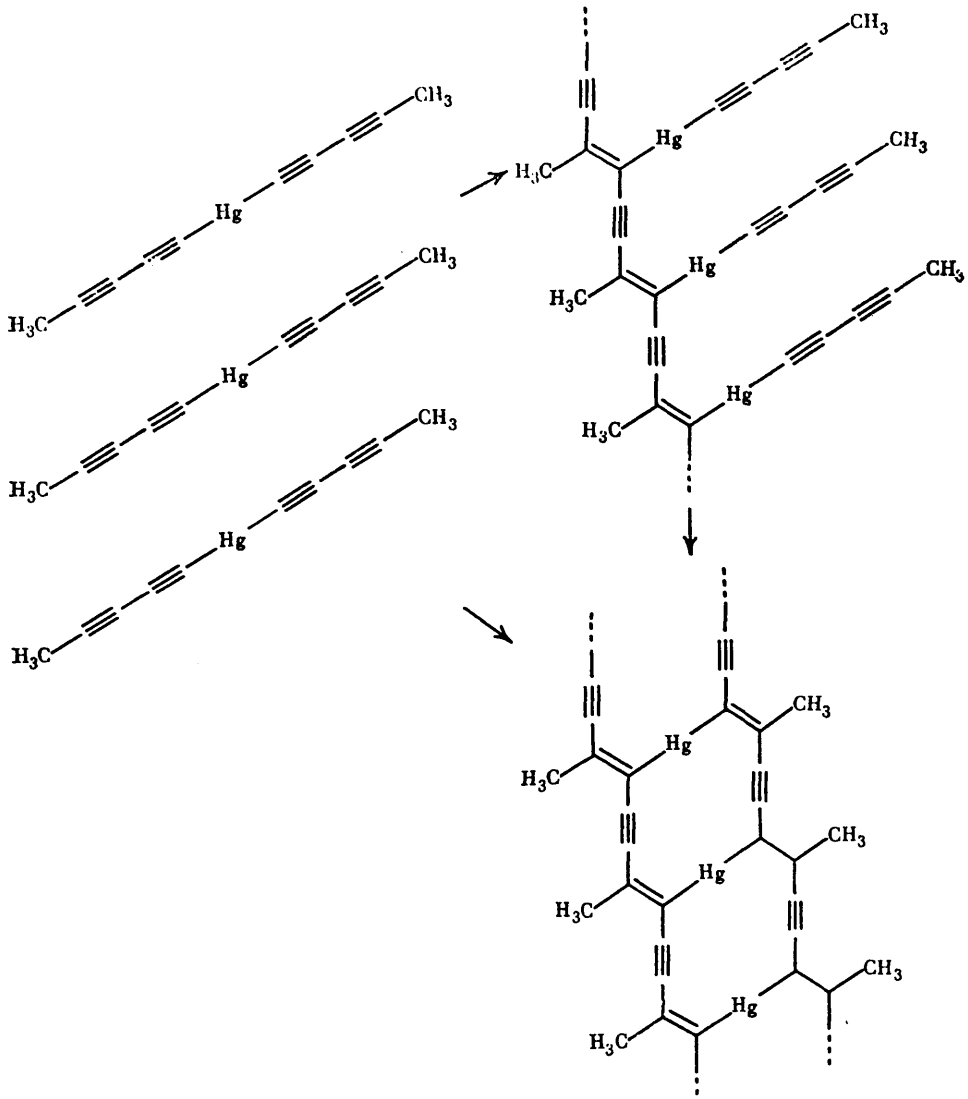


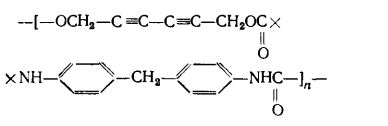
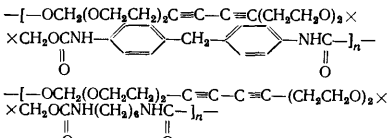
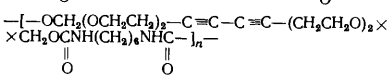
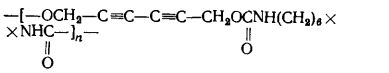
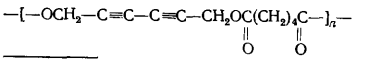
Figure 18.

A cross-linked polymer is formed under the influence of ^{60}Co γ-radiation in the crystals of these macromonomers via the topochemical polymerisation mechanism. The crystal unit cell parameters of the initial macromonomer and the cross-linked product have been determined (Table 3) and the possible polymer structure have been examined. It has been shown by ^{13}C NMR that the cross-linking is incomplete and that $=C-C\equiv C-C=$ bridges are formed during the reaction, since the signals characteristic of the butatrienes $C=C=C=C$ have not been observed in the range 200–220 p.p.m.[297]

An analogous reaction occurs also in less ordered polymeric systems. Thus the reactions of glycols containing DA groups with di-isocyanates or adipic acid dichloride gave rise to the corresponding soluble polyurethanes and a polyester (Table 9).[298,299] Owing to the presence of the reactive DA groups, the films made up of the heterochain polymer synthesised are coloured under the influence of ultraviolet light or heating to give red or orange tints with formation of a three-dimensional network. Polyurethanes based on hexamethylene di-isocyanate show the highest reactivity (Table 8), being coloured even when the specimens are merely pressed (at a pressure of 100–200 kg cm^{-2}).[299] Proof of the occurrence of the reaction in the more ordered regions is provided by the formation of a coloured gel from a precipitate of polyurethanes several seconds after the start of ultraviolet irradiation, while irradiation of solutions of these polymers leads to the appearance of only a weak brown colour after 30 min. It has been observed that the cross-linking of solid polymers is catalysed by radical initiators (benzoyl peroxide, azobisisobutyronitrile) and is inhibited by hydroquinone. Solutions of polymers do not exhibit this type of behaviour.[299]

The polyurethane $-[-NH(CH_2)_6-NH-\overset{\overset{O}{\|}}{C}-O-CH_2-(C\equiv C)_3-CH_2-O-\overset{\overset{O}{\|}}{C}-]_n-$, obtained from octa-2,4,6-triyne-1,8-diol and hexamethylene di-isocyanate, also gives rise to cross-linked products in yields of 75 and 13% respectively on heating (70 °C, 48 h) or ultraviolet irradiation (3 h).[300]

Table 9. The properties of heterochain polymers with the $-(C\equiv C)_2-$ groups in the main chain.[298,299]

Polymer	M.p., °C[1]	Appearance of colour	
		u.v. irradiation	heating
	~150	yellow	colourless
	~130	yellow	colourless
	138	purple	purple
	149	red	red
	~130	orange	yellow-red

[1]With decomposition; DSC, 32 K min^{-1}. [2]After 1 h at 110 °C.

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The data examined indicate a vigorous development of the research into the polymerisation of monomers with conjugated diacetylenic groups and also the wide-scale investigation of a whole set of specific properties of the polymers. The fact that the methods employed to obtain the polydiacetylenes are in essence the methods for the synthesis of polyconjugated polymers with small numbers of defects or no defects at all, which serve as effective models for the study of the physics of one-dimensional systems, is of special interest. The synthesis of tens of monomeric and oligomeric compounds of different classes, the study of their capacity for topochemical polymerisation, and the study of the structure of the polymerisation products formed revealed general rules obeyed by the polymerisation of compounds containing the $-(C\equiv C)_2-$ groups.

Nevertheless many problems, for example, the elucidation of the causes of the manifestiation of different reactivities of DA having similar electronic and steric structures, have remained unsolved. There is no doubt that further development of studies in the field of the solid-phase polymerisation of diacetylenes will lead to the creation of new types of oligomeric-polymeric materials with a specific structure and to a considerable expansion of their practical applications.

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Physical Chemistry of the Polycondensation of Polyfunctional Nucleophilic Compounds with Polycarboxylic Acid Derivatives

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The literature data on the kinetic and thermodynamic characteristics of the polycondensation of aromatic diols, diamines, tetramines, and their derivatives with tetracarboxylic acid dianhydrides and dicarboxylic acid dihalides in amide solvents are surveyed. Attention is concentrated on the analysis of the dependence of the physicochemical parameters of the polycondensation on the nature of the nucleophile and electrophile.
The bibliography includes 157 references.

CONTENTS

I. Introduction 594
II. The influence of solvents on low-temperature polycondensation processes 594
III. Charge-transfer complexes in polycondensation reactions 596
IV. Kinetic characteristics of the reactions of aromatic diols, diamines, and their derivatives with carboxylic acid dianhydrides and dihalides 598
V. Thermodynamics of the reactions 600
VI. Conclusion 605

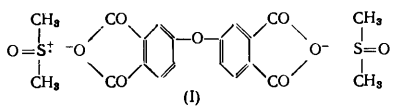
I. INTRODUCTION

Polycondensation in solution is nowadays widely used in industrial practice; as regards the industrial application of various polycondensation processes, this procedure is inferior only to polycondensation in the melt[1] (p.130). Aromatic polyamides, polyarylates, and other thermostable polymers are synthesised in solution by low-temperature polycondensation methods. This type of polycondensation began to be widely employed also in connection with the development of a two-stage method for the synthesis of polyheteroarylenes. In this synthesis, intermediate or so-called prepolymers are obtained in the first stage by the polycondensation of aromatic diamines and their derivatives with carboxylic acid dianhydrides or dihalides and are then converted into the final heterocyclochain polymers in the second stage of the process by solid-phase cyclodehydration at elevated temperatures.

Numerous studies of the low-temperature polycondensation processes in solution have been described in the literature; in the present review an attempt is made to give a systematic account and a survey of the results of these investigations.

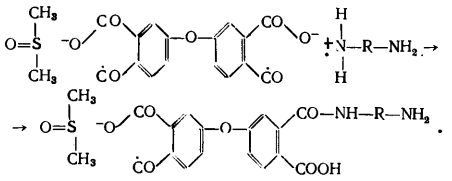
II. THE INFLUENCE OF SOLVENTS ON LOW-TEMPERATURE POLYCONDENSATION PROCESSES

In considering the mechanism of polycondensation in solution, many workers have suggested the formation of complexes between the polycarboxylic acid dianhydrides, and particularly dicarboxylic acid dihalides, with polar solvents.[2-8] For example, in a study of the reactions of benzidine, di(4-aminophenyl)methane, and di(4-aminophenyl)-ether with the dianhydride of oxydi(3,4-dicarboxybenzene) in solution in dimethylsulphoxide (DMSO), Kolesnikov et al.[8] suggested the formation of an anhydride–solvent adduct having the structure



(I)

The higher the nucleophilicity of the solvent, the more stable is the complex of this kind and the higher its concentration in solution. This can apparently explain the difference between the molecular weights of the polyamidoacids obtained in different solvents other conditions being equal, which has been observed in two investigations.[2,7] The above complex reacts with a diamine to form a new adduct:

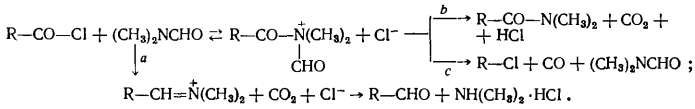


The transfer of one of the protons is responsible for the appearance of the amide bond and the formation of the polyamidoacid molecule.[5]

Boiko and Zhubanov[9] and Efimova et al.[10] pointed out the possibility of isolating such complexes, and presented the results of comparative studies of the rates of their interaction with diamines in polar solvents. Complexes of the dianhydrides of pyromellitic acid (PMDA) and 3,6-endoethene-9-bicyclo-2,4-octane-1,2,9,10-tetracarboxylicacid {3,6-(9-endoethene)bicyclo[2.4]octane-1,2,9,10-tetracarboxylic acid?} (AB) with DMSO, *NN*-dimethylformamide (DMF), and *NN*-dimethylacetamide (DMA) were chosen as the objects of study. The amine components selected were *m*-phenylenediamine (*m*-PDA), di(4-aminophenyl)ether (DAPE), and di(4-aminophenyl)methane (DAPM). Both in the case of AB and PMDA (Fig.1), the rate of the process is higher than the rate of interaction of the corresponding complexes. The polarity of the solvent forming part of the complex exerts an appreciable influence under these conditions on the reactivity of the complex. Analogous conclusions have been reached in other studies[10-12] where it was shown by infrared spectroscopy that polyamide–solvent complexes, whose nature influences greatly the molecular weight of the polymer formed, arise in solution in DMSO.

The studies of the reactions involving the synthesis of aromatic polyamides with carboxylic acid dichlorides in solvents of the amide type have shown that DMF is entirely unsuitable for such purposes. The impossibility of obtaining

high-molecular-weight compounds in this solvent[13,14] and the sharp decrease of the viscosity of the reaction solution following the preliminary dissolution of the dihalides in other amide solvents indicates the occurrence of side reactions, the main one being the interaction of the acid dihalide with the amide solvent.[4,15-17] This problem has been examined in fair detail in a number of investigations[16-18] in relation to the interaction of a series of acid dihalides with DMF. Thus it has been established[18] that two types of salts can be formed simultaneously in solution of the carboxylic acid chloride in DMF as a consequence of the attack by the electrophilic centre of the chloride on the oxygen or nitrogen atom in DMF:



If the acid chloride in which the R–C bond is weakened by structural features participates in the reaction of DMF, the corresponding salts of the acid chloride with DMF undergo decarboxylation (pathway *a*) or decarbonylation (pathway *c*), which lead to the formation of an aldehyde or a chloralkane. On the other hand, when the chloride of an acid incapable of decarboxylation is made to react with DMF, then transamidation takes place under more severe conditions and leads to the formation of the dimethylamide of the corresponding acid (pathway *b*).

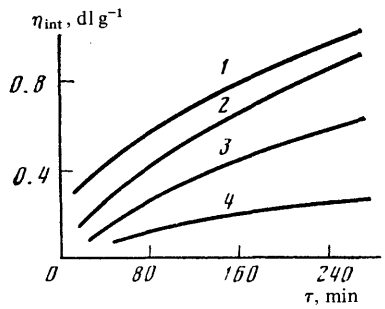
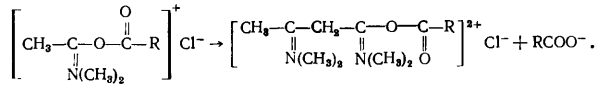


Figure 1. Dependence of the intrinsic viscosities of 0.5% DMF solutions of polyamidoacids obtained at T = 303 K via different reactions: 1) DAPE + AB; 2) DAPE + AB.DMSO; 3) DAPE + AB.DMA; 4) DAPE + AB.DMF (for the significance of the abbreviations, see text).[9]

It has been shown[19] in relation to the reaction of aniline with acid halides of different structure in DMF and DMA that at room temperature the acylation of aniline in DMF leads to the formation not only of the corresponding anilides but also of considerable amounts (up to 50%) of *NN*-dimethyl-*N'*-phenylformamidine, which means that, when the reaction was carried out in DMF, it proceeds via the formation of the intermediate adducts (I) (Scheme 1) of the acid halides with DMF and the adduct formation reaction is reversible. When aniline is added to the system, the equilibrium is displaced towards the formation of an adduct the rate constant for the interaction of which with aniline is much higher than that for the acylation of aniline by the acid halide.

The sharp decrease in the molecular weight of the polymer following the preliminary dissolution of the acid halides in DMF and other polar solvents has been explained[20] by the occurrence of side reactions other than those provided for by Scheme (1). For example, such a reaction may be the self-condensation of the adduct of DMA with the acid halide in accordance with the scheme[10]



It has been demonstrated convincingly[16] in relation to the acylation of aniline by the dichloride of isophthalic acid in solution in DMA that the amount of aniline which has not reacted increases the longer the acid dichloride has been kept in DMA and also with increase in the concentration of the salt in the same solvent. Analogous results have been obtained likewise in the analysis of the conditions governing the synthesis of polyterephthalamide based on di(4-aminophenyl)ether.

It is believed[21] that oligoanhydrides can be formed in amide–salt solvents together with other reactions.[14,15] In this case the presence of metal chlorides in solution in the synthesis of aromatic polyamides induces, together with an increase in the solubility of the polymers, an increase in the chemical reactivity of the solvent towards the initial monomers. This diminishes the molecular weight of the polymer formed.[16] In order to obtain polymers with a high molecular weight, it is therefore necessary to seek ways of diminishing the contribution of the reactions involving the formation of complexes between the monomers and the solvent. Thus the possibility of employing reactive solvents has been demonstrated.[1] It has been proposed[22] that the difluorides be used instead of the more reactive dichlorides. In order to diminish the extent of complex formation, it is recommended that preliminary dissolution of the acid dihalides in the amide solvent be avoided.[4]

The conditions in the polycondensation process in the synthesis of aromatic polyamides in amide solvents have been analysed by Ivanov et al,[23] who showed, in particular, that an increase of the rate at which the measured amount of the dichloride is introduced and especially the use of a solid dichloride leads to the formation of a polyamide with a higher molecular weight. Analogous results have been obtained by other workers,[24-26] who found that the polymer with the maximum molecular weight is obtained when the dry dianhydride is added to the solution of the diamine in small portions. Changing the order in which the reactants are added does not make it possible to obtain solutions with a sufficiently high viscosity. Similar conclusions were reached by other investigators[27-29] in relation to the polycondensation reaction of phenolphthalein with terephthalic acid dichloride in various solvents and also by Krongauz et al,[4] who investigated the reaction of the dihydrazide and dichloride of di(4-carboxyphenyl) ether in solution in hexamethylphosphoramide.

Thus, as already mentioned by Sokolov[1] (p.144), a quantitative estimate of the reactivity of the solvent in relation to the initial monomers is very important. Several methods for such estimations have been proposed in the literature. For example, in the study of the characteristics of the low-temperature polyesterification in a series of solvents[30-33] and also in the study of the reaction of 2,2-di(3-chloro-4-hydroxyphenyl)propane with terephthalic acid dichloride in the presence of triethylamine,[34] a tendency towards a decrease of the molecular weight of the polyarylates with increase of the dielectric constant of the solvent was established. Another method for estimations

of this kind involves the study of the reactions with participation of model compounds in various solvents. This problem has been examined in detail in a monograph,[1] where the results of studies of the condensation reactions of aniline with the dichlorides of isophthalic and terephthalic acids are analysed.

According to Sokolov,[1] the thermochemical method is very convenient for the quantitative estimation of the relative reactivities of solvents in complex formation reactions with the starting materials. As an example, Table 1 presents the enthalpies of solution ΔH^0_{solv} of isophthalic acid dichloride in organic solvents obtained in a number of studies.[22,35,36] The markedly different values of ΔH^0_{solv} at 298 K indicate comparatively strong interactions of isophthalic acid dichloride with amide solvents and conversely weak interaction with all others. The latter is indicated also by the results of a study of the viscosity (density)—composition diagrams[35] for the isophthalic acid dichloride–tetrahydrofuran (THF) system at 323 K. Both these relations are linear over the entire composition range, which indicates the absence of a specific interaction between the components. The intrinsic viscosities of solutions of polyisophthalamide obtained in DMA and DMF are 1.5 and 0.07 dl g^{-1} respectively (c = 0.5 wt.%, T = 293 K). These results agree with data[14] obtained in the study of the reaction of aniline with isophthalic acid dichloride in DMF and DMA. It has been shown[14] that, when the reaction is carried out in DMF, up to 70% of the monoanilide is formed, while in DMA the content of the monoanilide does not exceed 2–5% under the same conditions.

Table 1. The enthalpies of solution ΔH^0_{solv} of isophthalic dichloride in organic solvents at 298 K.[35]

Solvent	$-\Delta H^0_{solv}$, kJ mol^{-1}	Solvent	$-\Delta H^0_{solv}$, kJ mol^{-1}
Carbon tetrachloride	27.6	Tetramethylurea	18.0
Nitrobenzene	22.6	*N*-Methylpyrrolidinone	43.9
Methylene chloride	21.3	Dimethylacetamide	57.3
Toluene	20.9	Pyrrolidinone	157.7
Tetrachloroethane	18.4	Dimethylformamide	204.6
Tetrahydrofuran	16.7		

The interaction of acid chlorides with solvents of the amide type depends not only on the nature of the latter but also on the chemical structure of the initial dichloride.[35] The results of Sokolova and Sokolov[36] demonstrate, firstly, the higher reactivity of aromatic carboxylic acid dichlorides compared with those of aliphatic acids and, secondly, that the reactivity of aromatic acid halides in relation to amide solvents decreases in the sequence bromides > chlorides > fluorides. These results are satisfactorily correlated with data concerning the synthesis of polymers: the higher the enthalpy of reaction of the acid halide with the solvent, the lower the molecular weight of the polymer formed[1] (p.148).

It has been shown[37] that aromatic diamines are also capable of interacting with solvents to form side products. Thus, when a solution of di(3-amino-4-dydroxyphenyl) sulphone in DMA is heated, 87.5% of dimethylaniline relative to the theoretical amount is evolved. However, in solutions of benzidine, 3,3'-dihydroxybenzidine, and 2,2-di(3-amino-4-hydroxyphenyl)propane in DMA, dimethylamine in amounts of only 1.9, 2.15, and 5.4% respectively was detected after standing for 2 h at 298 K.[37] However, when DMA is capable of acylating the amino-group of the monomer, then this type of reaction should occur also in later stages of the polycondensation. This conclusion has been confirmed[37] in relation to the synthesis of poly[4,4'-dihydroxy-3,3'-(isophthalamido)diphenyl sulphone] in which not only chain termination but degradation of the polymer takes place.

As an illustration of the foregoing, one may also quote a study of the stability of the intrinsic viscosity of solutions of polyamidoacids based on pyromellitic anhydride and di(4-aminophenyl) ether[3] or bis(4-aminodiphenyl ether) of hydroquinone.[38] It was observed that the stability of the polyaminoacid in solution in DMF and DMSO is approximately the same and is significantly lower than in *N*-methylpyrrolidinone (MP). Comparison of the activation energies for the degradation of the polymers in various solvents (50 kJ mol^{-1} in DMF, 63 kJ mol^{-1} in DMSO, and 83 kJ mol^{-1} in MP) with data for the hydrolysis of the amide bond (75–85 kJ mol^{-1}) permits the conclusion[3,38] that the decomposition of polyamidoacids in amide solvents takes place preferentially as a result of the dissociation of the amide bond.

It follows from the foregoing that the choice of a solvent for the polycondensation of tetracarboxylic acid dianhydride or dicarboxylic acid dihalides with aromatic diamines and diols plays an extremely important role in the synthesis of the corresponding high-molecular-weight compounds. The presence of moisture in the reaction system must be very carefully monitored for such purposes. A detailed study[39] of the kinetics of the hydrolysis of isophthalic and terephthalic acid dichlorides has shown that in the temperature range 283–323 K they interact with water, which leads to the loss of the functional acid chloride groups. The presence of a definite amount of water in the solvent can therefore result in the cessation of polycondensation. Analogous effects of the hydrolysis of tetracarboxylic acid anhydrides have been observed also in the synthesis of polyamidoacids in amide solvents.[40]

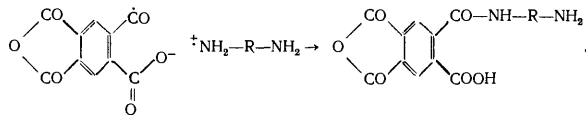
At the same time a number of workers[26,41–45] found in analysing various processes leading to the synthesis of polyamidoacids that the dependence of the molecular weight of the polymer formed on the concentration of water in the solvent always passes through an extremum. In other words, a small water content in the solvent (from 0.5 to 1.5 wt.%) not only does not lead to the hydrolysis of the initial dianhydride but also promotes an increase of the molecular weight of the polymer. The fact that, in conformity with the change in the equivalent conductance of aqueous solutions of aromatic acid dianhydrides on their interaction with the diamine, the rate of polycondensation is many times greater than the rate of hydrolysis agrees with this finding. The positive influence of the presence of water on the polycondensation has been explained[47] by the increased degree of swelling of the polymers in the presence of water, but no rigorous evidence for this is yet available.

III. CHARGE-TRANSFER COMPLEXES IN POLYCONDENSATION REACTIONS

Numerous studies[48–54] dealing with the synthesis and the interpretation of the electronic and infrared spectra of the solid reactants at 77–90 K and their solutions in non-polar

and highly polar solvents have been devoted to the donor-acceptor interaction in the systems carboxylic acid anhydrides–tertiary and primary amines. Analogous data have been obtained by other investigators[55–58] for the systems aromatic acid halides–tertiary and primary amines.

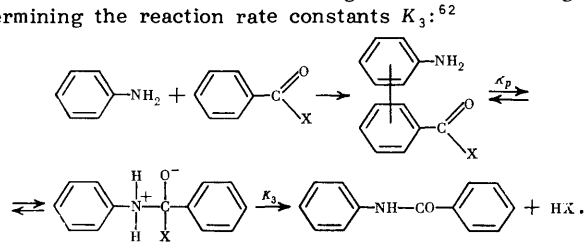
The results of these studies yield the conclusion that the reactions involved in the synthesis of polyamides, polyamidoacids, and their derivatives entail the formation of charge-transfer complexes (CTC) between the reactants. However, under the real conditions of low-temperature polycondensation (253–313 K) such complexes are unstable because their formation is followed by the rapid transfer of a proton from the amine to the anhydride group and the formation of an amide bond:



For a quantitative estimate of the electron-accepting and electron-donating properties of the reactants in acylation reactions, calculations have been made,[54,60–63] of the electron affinities and ionisation potentials of a series of carboxylic acid halides and anhydrides and aromatic diamines. The results of these investigations have been discussed in detail in a review[62] and we shall therefore quote here only the most important conclusions reached on their basis.

In the first place, the energy of charge transfer for the CTC of acid derivatives with the same electron donor increases linearly with their electron affinity. An analogous relation has been observed also for the CTC with the same electron acceptor, for example, with pyromellitic dianhydride for which the charge transfer energy varies in parallel with the variation of the ionisation potential of the aromatic amine.[62] The donor–acceptor interaction of amines with carboxylic acid derivatives, leading to the formation of CTC, is determined both by the electron-donating and electron-accepting properties of the reactants and by the polarity of the reaction medium. For example, bands of the *p*-phenylenediamine radical-cation and the chloranil radical-anion (total electron transfer) have been observed[64,65] in the study of the absorption spectra of this system in methanol.

It is believed[62] that the formation of the CTC of acid anhydrides with aromatic diamines is due mainly to the interaction of the aromatic rings (π-interaction). On the other hand, in the acylation of diamines by acid halides it was possible to detect the formation, together with the π-complex, of an adduct with a zwitter-ionic structure (a σ-complex) which is particularly stable in the case of tertiary amines. A mechanism has been proposed[62] for the acylation reaction including a CTC formation stage and the subsequent total electron transfer, which involves the appearance of a σ-complex in the system; the donor–acceptor properties of the reactant then determine the equilibrium constants K_p of the corresponding reactions. When the σ-complex is converted into the final products, the dissociation of the carbon–halogen bond is the stage determining the reaction rate constants K_3:[62]



Studies in which the energetics of the CTC formation reactions have been determined are therefore extremely interesting. Thus the thermodynamic functions of the CTC of dimethylaniline with phthalic, tetrachlorophthalic, and benzoic acids as well as the chlorides of benzoic, isophthalic, and phthalic acids in solution in acetonitrile have been calculated[66,67] (Table 2). In the CTC formation reactions involving acid chlorides the equilibrium constant is greater than for the formation of the complexes of the corresponding anhydrides. Since the enthalpies of both reactions are almost identical, the difference between the equilibrium constants is caused by the difference between the entropies of the above processes.[66]

Table 2. The energy characteristics of certain CTC formation reactions with participation of dimethylaniline.[66]

Acceptor	λ_{max}, μm	E_t, kJ mol^{-1}	$-\Delta H^0$ (298), kJ mol^{-1}	$-\Delta G^0$ (298), kJ mol^{-1}
TCPA	460	260.7	15.1±7.5	5.94
PA	375	318.8	8.4±6.3	3.51
BA	339	353.5	5.0±0.4	3.14
IPC	360	332.6	7.5±1.3	4.73
BC	338	354.0	4.6±0.8	5.65
PC	330	362.3	8.4±1.3	2.76

Notation. TCPA = tetrachlorophthalic acid anhydride; PA = phthalic anhydride; BA = benzoic acid anhydride; IPC = isophthalic acid dichloride; BC = benzoyl chloride, PC = phthalic acid chloride; E_t = electron transfer energy.

It is noteworthy that the calculated resonance energies and the contribution of the ionic structure of the complex in its ground state (which are 0.25 and 0.41% respectively in the case of benzoic acid anhydride and chloride, for example) did not confirm the conclusion[62] that there is a high contribution by the ionic structure. At the same time one of the principal postulates put forward by the above workers,[62] namely that the kinetics as well as the energetics of the CTC formation reactions and the electron affinity of the electron acceptor vary in parallel, has been confirmed,[66] because it has been found that in a series of anhydrides the decrease of the electron affinity of the acceptor is accompanied also by a decrease of the equilibrium constant for the CTC formation reaction.

Extensive information about the CTC of aromatic diamines with chloranil, which is similar to pyromellitic dianhydride as regards the character of its interaction with π-donors,[68] has been obtained.[57,69] It was found that the complex formation equilibrium constant diminishes with decrease of the basicity of the amine. In addition, a correlation has been observed between the thermodynamic characteristics of the CTC investigated and the rate constant for the reaction of the same diamine with pyromellitic dianhydride. The above workers[71] carried out a spectroscopic-kinetic study of the reaction of *m*-phenylenediamine with pyromellitic dianhydride and dichloropyromellitic dianhydride. The electron phototransfer and thermotransfer in model systems containing primary and substituted aromatic diamines and electron acceptors have been investigated. A mechanism for the elementary stage in the polycondensation reaction, which consists of successive electron and proton transfer from the amino-group to the partially positive centre of the dianhydride, has been proposed on the basis of the results.

Thus analysis of the literature data has shown that interaction involving the formation of CTC is an essential stage in polycondensation reactions with participation of aromatic diamines and carboxylic acid derivatives.

IV. KINETIC CHARACTERISTICS OF THE REACTIONS OF AROMATIC DIOLS, DIAMINES, AND THEIR DERIVATIVES WITH CARBOXYLIC ACID DIANHYDRIDES AND DIHALIDES

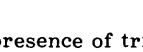
The first studies of the polycondensation reactions of aromatic diamines with tetracarboxylic acid dianhydrides already made it possible to establish the series of the relative reactivities of the corresponding nucleophiles[72,73] and electrophiles[72] on the basis of the results of measurements of the viscosities of the solutions of the polymers formed. The same method has been used[74-77] for the analysis of the reactivities of the bisphenols and aromatic acid dichlorides in polyesterification reactions. In particular, it has been shown[76] that the decrease in the reactivity of the dichloride not only diminishes the molecular weight of the polyarylate but also abolishes its temperature dependence.

The influence of the chemical structure of diamines and acid dianhydrides on the molecular weights of the polymers formed has also been examined by other investigators.[78,79] The reactivity of tetracarboxylic acid dianhydrides has been estimated[80] from measurements of the electron conductivities of their aqueous solutions. It has been suggested[81] that the comparative rates of dissolution of the monomers in organic solvents be used for the estimation of their reactivities. For the same purpose, the copolycondensation constants have been compared in a number of studies, in particular by Zhubanov et al,[82] which have been used to determine the relative reactivities of alicyclic tetracarboxylic acid dianhydrides. The reactivities of aromatic diamines have been estimated quantitatively[83-86] from the rate constants for the polycondensation with 1,6-hexamethylene diisocyanate in various solvents. It has been shown that the introduction of electron-accepting substituents into the diamine molecule lowers its reactivity and in many cases the reaction hardly proceeds.[84] As regards dianhydrides, particularly alicyclic acid dianhydrides, their reactivity is significantly influenced by steric factors.[73,87]

In view of the complexity of polycondensation processes, particularly as a consequence of the changed reactivity of the second reaction centre in bifunctional monomers after the first has reacted, many studies have examined the reactivity of the starting materials by using the reactions of model compounds. In one investigation[88] this has been done in relation to the reactions of aromatic amines with *p*-nitrobenzoyl chloride (or picryl chloride) while in another investigation[1] (p. 90) reactions of *p*-anisidine with acyl halides were used.

The reactivities of aromatic acid dichlorides in *p*-nitroaniline acylation reactions have been investigated[89] in solution in DMA at 298 K. It has been shown that the separation of the acid chloride groups by two benzene rings lowers appreciably the reaction rate constant compared with the amination of terephthalic acid dichloride. However, the introduction of powerful electron-accepting groups (for example, SO_2) between the benzene rings increases the rate constant for the above reaction. It is noteworthy that the reactivity of dinuclear acid dichlorides depends much less on the nature of the bridging group in a molecule than the reactivity of diamines with an analogous structure.[60,81,83,84]

The rate constants k_1 and k_2 for the reactions involving the successive addition of aniline derivatives to isophthalic and terephthalic acid dichlorides in various solvents have been determined[90] [see also Sokolov[1] (p. 24)]. It was found that in all cases $k_1 > k_2$. The reduced reactivity of the second COCl group is manifested to a greater extent by terephthalic acid dichloride. For the same acid dichlorides, k_1/k_2 increases with increase of the basicity of the amine and is independent of the nature of the solvent. At the same time in individual instances there is a possibility also of the opposite relation between k_1 and k_2 (Table 3).

Table 3. The rate constants for the reactions of terephthalic acid dichloride with the phenols 

in the presence of triethylamine (dioxan, 303 K).[91]

R	k_1, litre mol^{-1} s^{-1}	k_2, litre mol^{-1} s^{-1}	k_1/k_2	pK_a^*
CH_3	11.5±1.0	4.7±0.3	2.45	14.4
H	10.0±1.0	6.8±0.9	1.47	13.7
Cl	17±1	15±1	1.13	12.7
NO_2	48±2	62±3	0.77	10.1

*The ionisation constant of the phenol.

The acylation[92] of *o*-phenylenediamine by an equimolar amount of *m*-carbaboranedicarboxylic acid monochloride has been investigated[92] in solution in THF at 263 K in the presence of tertiary amines and the quantity $\alpha = k_2/k_1$, characterising the relative reactivities of the amino-groups in the *o*-phenylenediamine molecule, has been calculated from the equation quoted by Emanuel' and Knorre[93] (p. 194). It was found that in all cases $\alpha < 1$ and depends on the nature of the tertiary amine (for example, $\alpha = 0.15$ and 0.018 for reactions involving pyridine and trioctylamine respectively). The marked difference between the reactivities of the amino-groups in the presence of trioctylamine consists also in aromatic tetra-amines, which leads to the formation of linear polyaminoamides (PAA). In the presence of pyridine and quinoline the difference between the reactivities of the amino-groups diminishes ($\alpha = 0.11-0.15$), which results in the formation of soluble PAA with a branched structure. In the presence of triethylamine and dimethylaniline ($\alpha = 0.39$ to 0.47), insoluble cross-linked polymers are formed.[94]

Thus the synthesis of polybenzimidazoles involves difficulties associated primarily with the high probability of the cross-linking of the growing macrochains owing to the low reactivities of all four amino-groups in the tetra-amine molecule. It has been shown[95-97] that this phenomenon can be avoided by using for the reaction with acid dichlorides, aromatic bis(*N*-phenyl-*o*-phenylenediamines) or tetramines in which two amino-groups have been replaced by acetamido-groups.[98]

The possibility of employing indirect methods for the estimation of the reactivities of polycondensation monomers, for example, using the ionisation constants, the stretching vibration frequencies of the reacting bonds, and other properties, has been noted.[7] This postulate has been confirmed for the condensation of benzoyl chloride with aromatic amines[1] (p. 27).

The calculation of molecular diagrams by the LCAO-MO method in terms of the Hückel π-electron approximation has proved extremely useful for such purposes. Calculations of this kind have been carried out for aromatic diamines,[99]

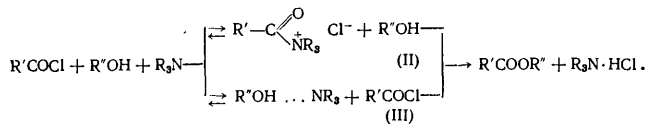
tetramines,[100] dicarboxylic acid bisamidrazones,[101] bisphenols,[102] and carboxylic acid dianhydrides[103] and dichlorides.[104] The calculations showed that the charges on the oxygen atoms in bisphenols and on the carbon atoms in acid dichlorides are linearly related to the Hammett substituent constants. In the case of amines, the electron densities at the nitrogen atom vary in parallel with the basicity of the amines. For example, the data of Bochvar et al[100] have been used to interpret the formation of linear polyaminoamidoacids;[105] the same data[100] agree with the ionisation constants of the tetramines quoted by Balyatinskaya et al.[106] The calculated energies of the lowest valence orbital of acid dianhydrides and their derivatives and the frontier electron densities of the carbonyl carbon atoms[103] made it possible to elucidate the detailed mechanism of acylation reactions, i.e. they determine the direction of nucleophilic attack.

Sokolov and co-workers[1] (pp. 28, 107, 147) were among the first groups of investigators who proposed a method for the estimation of the reactivities of diamines and acid dihalides from the enthalpies of their reactions with organic solvents (DMF, DMA, etc.) or an aqueous hydrochloric acid solution. The quantitative information obtained by this procedure makes it possible to select the reactants for the synthesis of polymers, since the higher the enthalpy of reaction of the acid dichloride with the solvent the lower the molecular weight of the polyamide formed in the corresponding reaction.

The reactivities of monomers depend to a large extent on the nature of the solvent chosen for polycondensation. This has been demonstrated convincingly in relation to the synthesis of poly-*m*-phenyleneisophthalamide[1] (p. 88) and also in the analysis of the kinetics of the acylation of *p*-nitroaniline by terephthaloyl chloride[89] in the following solvents: acetonitrile ($pK_a = 10.13$; $k = 0.03$ litre mol^{-1} s^{-1}); *N*-methylpyrrolidinone ($pK_a = 0.92$; $k = 1.80$ litre mol^{-1} s^{-1}); dimethylacetamide ($pK_a = 0.19$; $k = 2.90$ litre mol^{-1} s^{-1}).[89] Evidently the basicity of the solvent is a significant factor, which influences the rate of polycondensation reactions.

However, one must note that, whilst giving preference to monomers with a higher reactivity in polycondensation reactions, one must rigorously take into account the role of side reactions. Since the more reactive monomer is more actively involved in such reactions, in many instances this can lead to a decrease of the molecular weight of the polymer formed[1] (p. 89).

The most thoroughly investigated branch of the polycondensation kinetics is that of the high-temperature (423–483 K) polyesterification of dicarboxylic acid dichlorides with bisphenols in solution. For a comparatively large number of reactions, the rate constants and activation energies for the synthesis of polyarylates have been determined. The results of these studies are presented and discussed in the monograph of Korshak and Vinogradova[108] (chapter III). The problems of the kinetics and mechanism of the low-temperature condensation of the same reactant in the presence of tertiary amines (acceptor–catalytic polycondensation) have already been examined in detail in reviews.[109–111] In this review we shall only mention that fact that the mechanism of the acceptor-catalytic polyesterification can be represented by two "catalytic fluxes": nucleophilic [the formation of complex (II)] and general basic [the formation of complex (III)]:



The relative contributions of the above mechanism are determined mainly by the basicity of the tertiary amine employed and the acidity of the phenol. Increase in the acidity of the phenol and in the basicity of the tertiary amine creates conditions for reaction via the general base catalytic mechanism. Questions concerning the choice of the catalyst and of its influence on the side reactions in polycondensation processes and the properties of the polymers formed have been examined in very great detail in a review.[112] The kinetic aspects of the reactions in the low-temperature polycondensation of aromatic diamines with tetracarboxylic acid dianhydrides have been analysed in a number of investigations. The kinetics of the formation of polyamidoacid (PAAC) based on pyromellitic dianhydride (PMDA) and *m*-phenylenediamine in solution in DMF have been investigated.[113,114] The kinetics of the polycondensation of PMDA with dinuclear aromatic diamines in the same solvent have been discussed.[115] Quantitative information about the kinetics of the reactions of 9,9-di(4-aminophenyl)fluorene with a series of tetracarboxylic acid dianhydrides in solution in *N*-methylpyrrolidinone has been obtained.[116] The systematic investigations of the kinetics of the formation of DAAC based on the dianhydrides of tricyclodecenetetracarboxylic acids in solution in DMF have been carried out.[117–120] Certain postulates concerning the mechanisms of the above reactions have been published in other communications.[117,118,120,121] Analysis of the experimental results of the above studies permits the following conclusions.

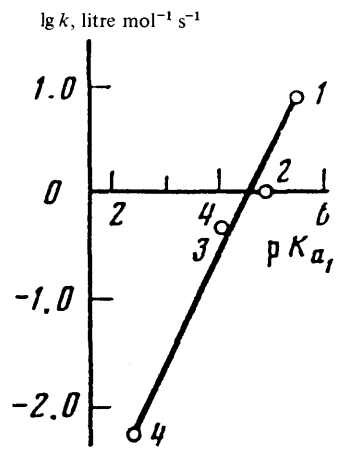


Figure 2. Dependence of the logarithms of the rate constants for the reactions of PMDA with amines on the logarithms of the first ionisation constants of the amines: 1) reaction with di(4-aminophenyl) ether; 2) reaction with *m*-phenylenediamine; 3) reaction with di(4-aminophenyl) sulphide; 4) reaction with di(4-aminophenyl) sulphone; 5) solvent—DMF; 298 K.[70]

Firstly, the rate constants for the polycondensation reactions of the same acid dianhydrides with different aromatic amines increases with increasing basicity of the amine (Fig. 2). In the reactions of the same diamine with different carboxylic acid dianhydrides the rate increases with increasing electrophilic character of the carbon atoms in the anhydride molecule. For example, according to

Vygodskii et al,[116] the rate constants for the polycondensation of 9,9-di(4-aminophenyl)fluorene at 298 K in solution in *N*-methylpyrrolidinone with dinuclear dianhydrides are 0.079, 0.49, and 1.70 litre mol^{-1} s^{-1} for the dianhydrides of tetracarboxylic acids derived from diphenyl ether, benzophenone, and diphenyl sulphone respectively.

Secondly, the reactivities of the dianhydrides of aliphatic and alicyclic acids are lower than those of the dianhydrides of aromatic acids, other conditions in the polycondensation reaction being equal. For example, the rate of reaction of di(4-aminophenyl)ether in solution in DMF with PMDA is 1000 times higher than the rate of polycondensation of the same diamine with the dianhydride of tricyclo[4,2,2,$0^{2,6}$]dec-7-ene-3,4,9,10-tetracarboxylic acid AB[70] and approximately 100 and 50 times greater than the rates of acylation of di(4-aminophenyl)ether by the dianhydrides of mesobutane-1,2,3,4-tetracarboxylic acid (MBTCA) and cyclopentane-1-*cis*, 2-*cis*, 3-*cis*-tetracarboxylic acid (CPTCA) in the same solvent.[121] On the other hand, the activation energies for the last two reactions[121] exceed by factors of 6 and 4.5 respectively the activation energy for the polycondensation of di(4-aminophenyl)ether with PMDA.[122]

Thirdly, the formation of polyamidoacids from aromatic diamines and acid dianhydrides consists of rapid (I) and slow (II) stages (Table 4). Whereas Koton[121] attributes this to the formation of monoacyl derivatives with a reduced basicity of the amino-groups in the first stage, Zhubanov et al[118] explain the above finding by the different reactivities of the dianhydride groups in asymmetric alicyclic acid dianhydrides relative to the reactions of diamines. For example, this can be caused by the different electron-donating properties of the cyclobutane and cyclohexane fragments and also by the shielding of one of the anhydride groups.[123]

Table 4. Kinetic parameters of the interaction of di(4-aminophenol) ether with AB[118] MBTCA, and CPTCA[121] (solvent—DMF; 298 K).

Dianhydride	Rate constant, litre mol^{-1} s^{-1}		E_a, kJ mol^{-1}	
	section I	section II	E_I	E_{II}
AB	$4.15 \cdot 10^{12}$	$4.18 \cdot 10^{-3}$	40.0±2.0	30.5±2.0
MBTCA	$(0.8 \pm 0.3) \cdot 10^{-1}$	$(3.1 \pm 0.5) \cdot 10^{-3}$	—	—
CPTCA	$(1.6 \pm 0.4) \cdot 10^{-1}$	$(3.6 \pm 0.5) \cdot 10^{-3}$	—	—

For the significance of the abbreviations, see text.

Nevertheless, one can agree with the view[121] that the onset of the growth of the macrochain in the synthesis of PAAC is associated with the formation of monoacyl derivatives of diamines and that the chain growth is caused by the preferential reactions of their functional groups. It has also been noted that the kinetics of the reactions involved in the synthesis of polyamidoacids can be successfully described taking into account their autocatalytic and equilibrium character.[120]

The kinetic features of the reactions involved in the single-stage polycondensation of diamines with tetracarboxylic acid dianhydrides have been elucidated in relation to the synthesis of polyimides. The molecular weights of the polymers obtained in solution are higher than those of the same polyimides synthesised by the two-stage method. The factors influencing the rate constants for the reactions involving the single-stage synthesis of polyimides are mainly the same as for the processes in the synthesis of polyamidoacids: the structure of the starting materials,[128,129] the nature of the solvent,[130] and the conditions in the polycondensation process.[113,124]

V. THERMODYNAMICS OF THE REACTIONS

The principal relations between the number-averaged degree of polycondensation $\bar{P}_n$ and the degree of reaction p, between $\bar{P}_n$ and the polycondensation equilibrium constants K_p, and between $\bar{P}_n$ and the molecular weight distribution of the linear polycondensation polymer have been obtained by Flory.[132] Later these postulates were analysed in detail in a number of investigations,[1,133–141] which showed that the study of the polycondensation thermodynamics is important because the equilibrium states in these processes determine the average degree of polycondensation, the molecular weight, and the molecular weight distribution of the polymer formed.

In connection with the development of the two-stage method for the synthesis of polyheteroarylenes, special attention is devoted in the literature to the low-temperature polycondensation processes in solution. Much quantitative information about the thermodynamics of the reactions of phthalic anhydride (PA) with aniline, which models the formation of polyamidoacids, has been published.[142]

The results permit the conclusion that the equilibrium constants for the acylation reaction depend on the structure of the starting materials: whereas the reactions of phthalic anhydride with *p*-nitroaniline and of PMDA with di(4-aminotetrafluorophenyl) ether hardly occured at 313 K, the equilibrium in the phthalic anhydride–aniline and PMDA–*p*-phenylenediamine systems is markedly displaced towards the formation of *o*-carboxyamides under the same conditions. The introduction of the electron-donating substituents CH_3, CH_3O, $(CH_3)_2N$ in the *para*-position in the aniline molecule entails an even greater increase of the equilibrium constants, i.e. its parallel variation with the basicity of the amine employed is observed.

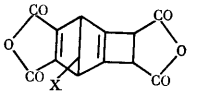
Comparison the equilibrium constants for the same reaction in different solvents has shown that the equilibrium shifts to the right with increasing basicity of the solvent. Thus, on passing from acetonitrile to THF, K_p increases almost by a factor of 10, while in dimethylsulphoxide and diemthylacetamide this constant exceeds 1×10^5. The influence of the basicity of the medium is reflected also in the enthalpy of the process, which amounts to −48.0 kJ mol^{-1} in acetonitrile and −54.5 kJ mol^{-1} in THF. This is believed[142] to be related to the association of the carboxy-groups of the products with the solvent molecules, which has been confirmed by the infrared spectroscopic data for a series of model compounds.

Analogous data concerning the influence of the solvent on the enthalpy of the reaction of phthalic anhydride with 4-aminodiphenyl ether, which models the synthesis of PAAC, were obtained later.[143]

Zhubanov and co-workers[119,144–147] used infrared spectroscopy to investigate the polycondensation reactions of aromatic diamines with the dianhydrides of tricyclodecenetetracarboxylic acid at 298 K in DMF; the results are compiled in Tables 5 and 6. The reactivity series of the dianhydrides has been proposed on the basis of the decreasing absolute Gibbs energy of the reaction (ΔG_r^0, Table 5). The aromatic

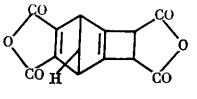
diamines investigated can be arranged in a series, based on the absolute values of ΔG_r^0 (298) for the polycondensation reaction with a specific dianhydride (Table 6), which agrees with the series based on their first ionisation constants.

Table 5. Thermodynamic parameters of the reactions of di(4-aminophenyl)ether with the dianhydrides.[146]



X	$-\Delta H_r^0$, kJ mol^{-1}	$-\Delta G_r^0$, kJ mol^{-1}	$-\Delta S_r^0$, kJ mol^{-1} K^{-1}	K_c, litre mol^{-1}
F—	114.5	22.7	308	9700
Cl—	109.1	21.8	293	6600
H—	122.4	16.6	356	807
H_3C H_3C CH—	122.7	13.7	365	274
$H_3C-C(CH_3)_2-$	136.3	12.2	417	139
H_3C H_3C CH—CH_2—	117.7	11.8	356	121

Table 6. Thermodynamic parameters of the reactions of aromatic diamines with the dianhydride.[146]



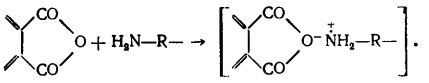
Diamine	$-\Delta H_r^0$, kJ mol^{-1}	$-\Delta G_r^0$, kJ mol^{-1}	$-\Delta S_r^0$, J mol^{-1} K^{-1}	K_c, litre mol^{-1}
p-Phenylenediamine	128.2	18.9	367	2075
m-Phenylenediamine	99.0	16.4	277	746
Di(4-aminophenyl)methane	114.4	16.5	329	790
Di(4-aminophenyl)sulphide	79.8	14.1	221	302
Di(4-aminophenyl)sulphone	—	2.7	—	3

We shall next consider the results of the study of the thermodynamics of the polycondensation reactions of tetracarboxylic acids dianhydrides with aromatic diamines, tetraamines, and their derivatives in solution.[148-157]

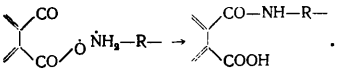
1. Thermodyamics of the Polycondensation Reactions of Tetracarboxylic Acid Dianhydrides with Aromatic Diamines

Tables 7–9 present the results of the determination of the enthalpies of the reactions of the dianhydrides of oxybis-(benzene-3,4-dicarboxylic) acid (OBBDA) and PMDA with mononuclear and dinuclear diamines and also with aromatic diamines containing benzimidazole and triazole groups.

The synthesis of poly(*o*-carboxy)amides proceeds via a bimolecular reaction involving the acylation of amines whose mechanism includes the nucleophilic attack on the amino-group, leading to the opening of the anhydride ring with formation of the amide bond. The attack by the nucleophile on the partially positive centre of the dianhdyride terminates in electron transfer (complete or partial depending on the dielectric constant of the medium) to the acceptor (the dianhydride):



However, this system is unstable, because its formation is followed by the rapid proton transfer from the amine to the anhydride group and by the formation of the amide bond:



This process is accompanied by the dissociation of the N–H and C–O bonds in the diamine and dianhydride molecules respectively and by the formation of new bonds (O–H, C = O, and C–N) in the polymer macromolecule. The fact that interaction of various diamines with the same dianhydrides results in the evolution of unequal amounts of heat is due primarily to the different nucleophilicites of the initial nucleophiles. On the other hand, the nucleophilicities of the amines investigated, determined by the presence of the unshared electron pair at the nitrogen atom of the amino-group, depend on the basicity of these substances.

The present authors[150,151] have attempted to relate the enthalpies of the synthesis of poly(*o*-carboxy)amides to the basicities of the initial diamines. Indeed, the higher the basicity of the amine, i.e. the higher the electron density at the nitrogen atom of the amino-group, the easier the electron transfer to the partially positive centre of the anhydride. This leads in its turn to a relatively greater deficiency of electron density at the nitrogen atom of the amino-group, i.e. promotes the appearance of an excess positive charge. The latter promotes the polarisation of the N–H bond in the amine and facilitates the abstraction of a proton from the amino-group.

Thus an increase of the basicity of the amine diminishes the dissociation energy of the N–H bond in the amine. Since the enthalpy of the chemical reaction is determined by the algebraic sum of the energies of the bonds which have been ruptured and formed, the above fact should diminish the enthalpy with increasing basicity of the amine, bearing in mind that the energies of the other bonds indicated above vary to a lesser extent with the chemical nature of the amine in reactions with the same dianhydride. Indeed, linear relations between the enthalpies and the logarithms of the first ionisation constants of aromatic diamines have been observed for their reactions with OBBDA and PMDA.[151-153,156]

$$\Delta H_r^0(298) = A + B \cdot pK_{b_1}.$$

For the reactions of OBBDA with mononuclear diamines, the quantities ($-A$) and B are 203.0 ± 0.8 and 10.5 ± 0.3 respectively; for the reactions of OBBDA with dinuclear diamines the corresponding quantities are 969.0 ± 1.0 and 89.1 ± 0.8. Finally, the same parameters for the reactions of dinuclear diamines with PMDA are 934.0 ± 1.0 and 87.7 ± 0.7.

The above conclusions agree with the results quoted in Fig. 3, where the dependence of the enthalpies of the polycondensation of four dinuclear diamines with OBBDA and PMDA on the stretching vibration frequency of the amino-groups is presented.[153] On this basis, we suggest that an increase of the stretching vibration frequency indicates an increase of the N–H bond energy in the sequence di(4-aminophenyl) ether < 4,4′-diaminobiphenyl < di(4-aminophenyl) disulphide < di(4-aminophenyl)sulphone. The enthalpies of the corresponding polycondensation reactions vary in the

same direction. For example, the introduction of an electronegative substituent between the benzene rings in the amine molecules (oxygen bridge) diminishes the enthalpy of reaction in solution by 8.0 ± 1.5 kJ mol^{-1} (Tables 8 and 14). The introduction of the electron-accepting CO or SO_2 groups between the benzene rings increases the enthalpy of reaction in solution in DMF by 15 ± 5 and 23 ± 2 kJ mol^{-1} respectively (Tables 8 and 14).

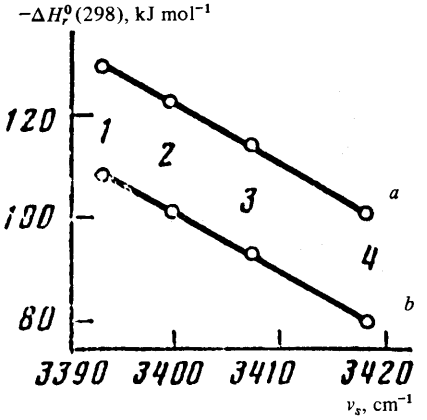
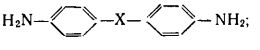


Figure 3. Dependence of the enthalpies of polycondensation of aromatic diamines with OBBDA (*a*) and PMDA (*b*) on the stretching vibration frequency ν_S of the NH_2 groups of the diamines[153]



X = *1*) -O-; 2) -S-S-; 3) $-SO_2-$.

Table 7. The enthalpies of polycondensation reactions of OBBDA with monoculear aromatic diamines (solvent—DMF; 298 K).[157]

Diamine	pK_{b_1} (H_2O)	$-\Delta H_r^0$, kJ mol^{-1}
1,4-Diaminoxylene	7.35	125.9±4.2
p-Phenylenediamine	7.96	119.7±0.4
m-Phenylenediamine	9.12	108.0±1.3
o-Phenylenediamine	9.48	103.3±2.1

In the case of the *para*- and *meta*-derivatives of amines, the lower enthalpy of the polycondensation of the latter with OBBDA refers respectively to *p*-phenylenediamine (−119.7 and −108.0 kJ mol^{-1}, Table 7), bis(*o*-aminophenyl)-*p*-benzoylene-2,2-bistriazole (−83.7 and −95.4 kJ mol^{-1}, Table 9), and the bisamidrazone of terephthalic acid (−116.3 and −128.0 kJ mol^{-1}, Table 9); the corresponding enthalpy difference is 11.7 kJ mol^{-1} in all cases under these conditions.

A linear relation has been established between the enthalpies of polycondensation of aromatic diamines with PMDA in solution in DMF and the logarithms of the rate constants for the same processes:[153]

$$\Delta H_r^0(298),\ (\text{kJ mol}^{-1}) = (-102.0 - 8.45 \lg K) \pm 1{,}0,$$

where K are the rate constants for the corresponding polycondensation reactions expressed in litre mol^{-1} s^{-1}. From this it follows that the variation of the enthalpy of the above reaction with the nature of the amine is correlated with the variation of the activation energy for the reaction.

Table 8. The enthalpies (kJ mol^{-1}) of the reactions of OBBDA, PMDA, and phthalic anhydride (PA) with the diamines $H_2N-C_6H_4-X-C_6H_4-NH_2$ (solvent—DMF; 298 K).[150]

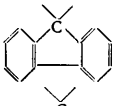
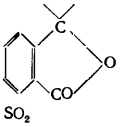
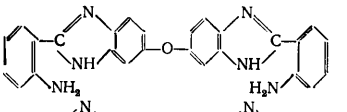
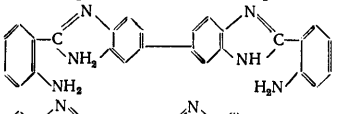
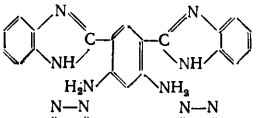
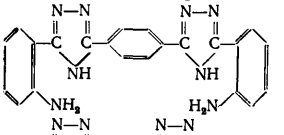
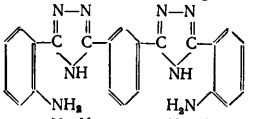
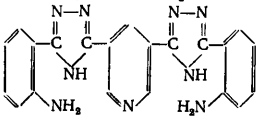
X	pK_{b_1}	pK_{b_2}	$-\Delta H_r^0$		PA		$\Delta H_1^0/\Delta H_2^0$
			OBBDA	PMDA	$-\Delta H_1^0$	$-\Delta H_2^0$	
CH_2	9.42	11.65	130.1±1.7	108.9±3.2	68.6	62.3	1.10
O	9.42	11.70	128.9±1.3	108.0±0.8	69.9	62.8	1.11
O	9.45	11.90	127.6±1.3	105.9±0.8	68.2	60.7	1.12
—	9.52	12.12	123.0±1.3	100.8±1.3	67.4	57.7	1.17
S	9.53	—	120.8±2.5	99.6±1.3	—	—	—
S—S	9.58	—	115.2±2.5	94.1±1.3	—	—	—
CO	9.69	13.42	105.4±1.7	85.0±0.8	61.9	31.4	1.97
	—	—	102.5±1.3	81.5±2.5	—	—	—
	—	—	101.5±1.3	80.5±2.5	—	—	—
SO_2	9.75	13.57	88.0±2.1	79.5±2.1	60.3	28.5	2.12

Table 9. The enthalpies of the polycondensation reactions of OBBDA with aromatic diamines containing benzimidazole and triazole rings (solvent—DMF; 298 K).[149,150]

Diamine	$-\Delta H_r^0$, kJ mol^{-1}
	147.3±4.2
	109.6±1.3
	92.1±2.9
	95.4±1.3
	83.7±2.1
	83.7±2.1

On the basis of the kinetic studies of the reactions of di(4-aminophenyl) ether with carboxylic dianhydrides, it has been suggested[121] that the synthesis of poly-(*o*-carboxy)-amides in solution in polar solvents proceeds via a stage involving the formation of monoacyl derivatives. It is therefore of interest to compare the enthalpies of the reactions for the successive addition of two moles of phthalic anhydride (PA) to one mole of the corresponding diamine. It follows from Table 8 that, for the reactions involving the addition of the second mole of PA to the diamine, $\Delta H_r^0(298)$ is in all cases smaller in absolute magnitude than the analogous values for the reactions of the first mole of PA with the initial diamine: $\Delta H_1^0 > \Delta H_2^0$. It has also been established[154] that ΔH_1^0 and ΔH_2^0 vary in parallel with the variation of the ionisation constants of the amines pK_b, namely for the first and second anhydride addition reactions the following relations have been obtained respectively:

$$\Delta H_1^0, \text{ (kJ mol}^{-1}) = (-338.4 + 28.5 \cdot pK_{b_1}) \pm 1.0 ;$$
$$\Delta H_2^0, \text{ (kJ mol}^{-1}) = (-286.2 + 18.9 \cdot pK_{b_2}) \pm 2.5.$$

Since in practice polyamidoacids are synthesised by adding the solid dianhydride to a solution of the diamine, we shall consider the thermodynamic characteristics of the dissolution of a series of dianhydrides in DMF. These results, which are presented in Table 10, show that the affinity of tetracarboxylic acid dianhydrides for DMF diminishes in the sequence PMDA > TBBDA > OBBDA.

Table 10. Thermodynamic parameters of the dissolution of dianhydrides in DMF at 298 K.[150]

Dianhydride	ΔH^0_{solv}, kJ mol^{-1}	$-\Delta G^0_{solv}$, kJ mol^{-1}	ΔS^0_{solv}, J mol^{-1} K^{-1}
PMDA	—12.96	100.5	288.7
TBBDA	—5.02	96.0	299.2
OBBDA	12.55	92.0	351.5

By adding together the enthalpies of solution of PMDA and OBBTA in DMF to the enthalpies of mixing of the solutions of the dianhydride and a diamine (Table 8), we obtain the enthalpy of reaction of the crystalline dianhydride with the solution of the diamine. Linear relations obtained from calorimetric data for the reactions of mononuclear diamines with crystalline OBBDA are presented below for the calculation of the enthalpies of such reactions of PMDA or OBBTA with other diamines from the enthalpies of reaction of the same anhydrides with the amines which we have investigated:[151–153,156]

$$\Delta H_r^0(298), \text{ (kJ mol}^{-1}) = (-182.1 + 9.48 \cdot pK_{b_1}) \pm 2.0.$$

For the reactions of dinuclear aromatic diamines with a crystalline OBBDA, we have

$$\Delta H_r^0(298), \text{ (kJ mol}^{-1}) = (-953.4 + 88.74 \cdot pK_{b_1}) \pm 2.5.$$

For reactions of dinuclear aromatic diamines with crystalline PMDA, we have

$$\Delta H_r^0(298), \text{ (kJ mol}^{-1}) = (-956.5 + 87.67 \cdot pK_{b_1}) \pm 1.0.$$

Analysis of the enthalpies presented in Table 8 for reactions carried out by mixing solutions of the starting materials established a linear relation between the enthalpies of polycondensation of OBBDA and PMDA with the same amine in DMF:

$$\Delta H_r^0(298, \text{OBBDA}) \text{ (kJ mol}^{-1}) = [-20.2 + 1.0 \Delta H_r^0(298, \text{PMDA}) \pm 1.5.$$

The relation obtained makes it possible to estimate reliably the enthalpy of reaction of a specific amine with one dianhydride from the known enthalpy of polycondensation of the same diamine with another dianhydride. An analogous relation has been obtained also for the enthalpies of polycondensation of the same amines with OBBDA and PMDA by adding the solid dianhydrides to a solution of the diamine in DMF:

$$\Delta H_r^0(298, \text{OBBDA}) \text{ (kJ mol}^{-1}) = [5.4 + 1.0 \times \Delta H_r^0(298, \text{PMDA}) \pm 1.5.$$

The entropies and Gibbs free energies of two processes of the type discussed have been determined calorimetrically for the reactions of OBBDA with di(4-aminophenyl)ether (DAPE) and di(4-aminophenyl) sulphone (DAPS) in DMF.[152] The above polycondensation reactions have been chosen because they are characterised by the maximum and minimum enthalpies respectively for the series of diamines investigated, which have been used to synthesise polyamidoacids. The results presented are listed in Table 11. It follows from these data that the entropies of the reactions investigated are negative and increase in absolute magnitude with increasing temperature. In contrast to ΔH_r^0, ΔS_r^0 is virtually the same for both processes. Consequently the enthalpies of the above processes are the factor which determines the differences between the Gibbs free energies of the acylation of the diamines by the same dianhydride.

Table 11. Thermodynamic parameters and equilibrium constants of the reactions of OBBDA with DAPE and DAPS (solvent—DMF; 101.325 kPa).[152]

T, K	$-\Delta H_r^0$, kJ mol^{-1}		$-\Delta S_r^0$, J mol^{-1} K^{-1}		$-\Delta G_r^0$, kJ mol^{-1}		K_c	
	DAPE	DAPS	DAPE	DAPS	DAPE	DAPS	DAPE	DAPS
240	114.0	69.0	114.0	95.0	87.5	46.5	$1 \cdot 10^{19}$	$1 \cdot 10^{10}$
260	122.0	80.0	145.0	139.0	84.5	44.5	$1 \cdot 10^{17}$	$8 \cdot 10^{8}$
280	129.5	88.0	175.0	169.0	80.5	41.5	$1 \cdot 10^{15}$	$4 \cdot 10^{7}$
300	129.0	88.0	191.5	190.5	72.0	31.0	$4 \cdot 10^{12}$	$3 \cdot 10^{5}$

It follows from the analysis of the dependence of ΔG_r^0 on T that the reactions of DAPE and DAPS with OBBDA in DMF are thermodynamically allowed over the entire temperature range and are characterised by high equilibrium constants. Presumably the equilibrium constants for other diamines at 298 K are also in the range 10^5–10^{12}. Thus the equilibria in the syntheses of poly(*o*-carboxyl)amides are almost completely displaced towards the formation of the polymers. With increase of temperature, their equilibrium constants diminish in conformity with the principle of the displacement of chemical equilibrium.

2. Thermodynamics of the Reactions of the Dianhydrides of Tetracarboxylic Acids with Aromatic Tetramines and Their Derivatives

Table 12 presents the enthalpies of polycondensation of OBBDA with certain bisamidrazones of dicarboxylic acids in dimethyl sulphoxide (DMSO) at 298 K. The enthalpies of the reactions involving the successive addition of two moles of PA to one mole of the corresponding bisamidrazone (Table 12) have also been determined. As in the reactions of PA with aromatic diamines (Table 8), the $\Delta H_r^0(298)$ values for the addition of the second mole of PA to the bisamidrazone are in all cases smaller in absolute magnitude than the analogous value for the reactions of the first mole of PA with the initial bisamidrazone. The difference between the enthalpies of addition at different stages of the process is greater for the bisamidrazone of terephthalic acid than for the bisamidrazone of isophthalic acid.

Table 12. The overall enthalpies of polycondensation of OBBDA with acid bisamidrazones in DMSO and the enthalpies (ΔH_1^0 and ΔH_2^0) of the subsequent addition of two moles of PA to one mole of the bisamidrazone.[150]

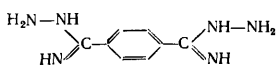
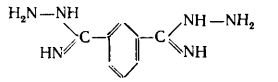
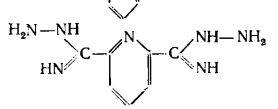
Bisamidrazone	$-\Delta H_r^0$ (298), kJ mol^{-1}	$-\Delta H_1^0$, kJ mol^{-1}	$-\Delta H_2^0$, kJ mol^{-1}	$\Delta H_1^0/\Delta H_2^0$
	128.0±1.7	75.7	46.4	1.63
	116.3±2.1	72.0	49.4	1.46
	111.3±2.1	69.5	50.2	1.38

Table 13 lists the values of ΔH_r^0 (298) for the reactions of OBBDA with tetramines. The introduction of electron-accepting substituents, for example, phenyl groups, into the tetramine molecule increases ΔH_r^0 (298 K), which agrees with the above hypothesis concerning the relation between the enthalpies of reaction of the dianhydrides with amines and the basicity of the latter. In particular, such a relation has been established in the following form for the tetramines which we have investigated:

$$\Delta H_r^0(298),\ (\text{kJ mol}^{-1}) = (-302.7 + 13.8 \cdot pK_{b_1}) \pm 2.5.$$

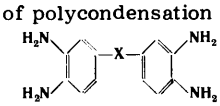
The ΔH_r^0 (298) for the reactions of tetra-aminobiphenyl and its phenyl-substituted analogue with OBBDA and also the ΔH_r^0 (298) for the polycondensation of bis(diaminophenyl) sulphone and its phenyl-substituted derivative with OBBDA differ by ~27 kJ mol^{-1}. The enthalpies of polycondensation of the phenyl-substituted tetramines with OBBDA in solution in DMF then vary in parallel with the variation of the ionisation constants of the amines in the same solvent:[151]

$$\Delta H_r^0(298),\ (\text{kJ mol}^{-1}) = (-354.2 + 19.5 \cdot pK_{b_1}) \pm 3.5.$$

An analogous relation has been obtained also for the reactions of phenyl-substituted tetramines with one mole of PA in DMF:

$$\Delta H_1^0(298),\ (\text{kJ mol}^{-1}) = (-127.9 + 5.2 \cdot pK_{b_1}) \pm 1.0.$$

where the experimental ΔH_1^0 (298) are −76.1, −62.8, and −56.5 kJ mol^{-1} for the phenyl-substituted derivatives of tetra-aminobenzene, tetra-aminobiphenyl, and bis(diaminophenyl) sulphone respectively.[151]

Table 13. The enthalpies (kJ mol^{-1}) of polycondensation of OBBDA with the aromatic tetramines  (solvent—DMF; 298 K; p = 101.325 kPa).[150]

X	pK*	$-\Delta H_r^0$ (298)	X	pK	$-\Delta H_r^0$ (298)
O	11.31	145.6±1.7	—	11.80	136.4±2.1
CH_2	11.58	142.3±0.4	CO	12.87	124.7±0.4
O—Ph—O	11.75	141.0±0.4	SO_2	13.66	115.4±0.4

*The ionisation constants of the tetramines in DMF have been determined by Balyatinskaya et al.[106]

Table 14. The entropies and Gibbs free energies of the polycondensation reactions of BDAPE with acid dianhydrides (solvent—DMF).[151]

T, K	$-\Delta S_r^0$, J mol^{-1} K^{-1}				$-\Delta G_r^0$, kJ mol^{-1}			
	TBBDA	OBBDA	BPDA	PMDA	TBBDA	OBBDA	BPDA	PMDA
240	28.0	73.0	31.5	10.5	171.5	131.8	131.8	106.7
260	33.5	75.5	33.5	17.0	169.5	131.8	129.7	106.7
280	42.0	75.5	42.0	23.0	167.4	129.7	127.6	104.6
300	52.0	77.5	48.0	33.5	165.3	127.6	125.5	102.5

It follows from the above conclusions concerning the thermodynamics of the polycondensation reactions of tetracarboxylic acid dianhydrides with aromatic diamines and their derivatives that a change in the nature of the electron acceptor in the reactions of the same nucleophile with different dianhydrides should exert a significant influence on the enthalpies of formation of the polymers. The determination of ΔH_r^0 (298) for the reactions of bis(3,4-diaminophenyl) ether (BDAPE) with various tetracarboxylic acid dianhydrides in solution in DMF established that in such cases an increase of the strength of the corresponding acid entails an increase of the absolute enthalpy of polycondensation of the dianhydrides with the same tetramine. The fact that the absolute value of ΔH_r^0(298) for the reaction of BDAPE with OBBDA is greater than the corresponding value for the reaction of BDAPE with the dianhydride of benzophenone-3,3′-4,4′-tetracarboxylic acid (BPDA) (−145.6 and −139.3 kJ mol^{-1} [157]) is associated with the fact that the addition of the first anhydride group in the case of BPTA results in a more marked decrease of the enthalpy of addition of the second

anhydride group than for OBBDA:[157]

	$-\Delta H_1^0$, kJ mole^{-1}	$-\Delta H_2^0$, kJ mol^{-1}	$\Delta H_1^0/\Delta H_2^0$
BPDA	60.2	33.1	1.8
OBBDA	57.7	40.2	1.4

The entropies and Gibbs free energies of reaction of a number of dianhdyrides with BDAPE in solution in DMF have been determined (Table 14). As for the polycondensation of dianhydrides with aromatic diamines (Table 11), the entropies of reaction of BDAPE with various dianhydrides are negative at all temperatures. On the other hand, the absolute value of ΔS_r^0 is comparatively small and the entropy component ΔS_r^0 in the expression for the Gibbs free energy is 10–15% of the enthalpy component.[151] The results obtained make it possible to set up the following reactivity series for the dianhydrides in their reactions with aromatic amines: TBBDA > OBBDA > BPDA > PMDA.

The equilibrium constants for the reactions investigated permit the conclusion that the equilibrium is in all cases almost fully shifted towards the formation of the corresponding polymer.

VI. CONCLUSION

Examination of the data described makes it possible to note the following points. The reactions of aromatic diamines, diols, and their derivatives with carboxylic acid dianhydrides and halides in amide solvents proceed in two stages. The first functional groups of these substances interact in the first stage and the activation energy is 30–40 kJ mol^{-1}. The second functional groups of the initial monomers react in the second stage and the rate constant for their interaction is lower by two–three orders of magnitude than the analogous value for the first stage, while the activation energy for the second stage is 20–30 kJ mol^{-1}.

The introduction of electrophiles into the solvent before adding the nucleophile leads to a significant decrease of the molecular weight of the polymer formed compared with that obtained when the reactants are added to the solvent in tbe opposite order or simultaneously.

The transition state in the polycondensation reactions is a charge-transfer complex whose formation can be detected, for example, from the infrared spectra of the solutions at low temperatures (~180 K). The processes involving the formation of such complexes are exothermic and their enthalpies amount to several tens of kJ mol^{-1}; their entropies are negative and amount to tens of J mol^{-1} K^{-1}, which leads to Gibbs free energies ranging from −2 to −10 kJ mol^{-1}.

The enthalpies of the polycondensation reactions with formation of aromatic polyesters, polyamides, or their *ortho*-derivatives in solution are negative and are linearly related to the logarithms of the ionisation constants of the nucelophiles. The entropies of the polycondensation reactions in solution are negative and depend only slightly on the nature of the reactants or are comaratively small in the given reaction series. The variation of the Gibbs free energies of the polycondensation processes with the chemical nature of the amine or the dianhydride is therefore determined mainly by the simultaneous variation of the enthalpy of the process, whose magnitude is significantly influenced by the variation of the dissociation energy of the N–H chemical bond (or the C–O or C–Cl bonds) in the starting materials of the above reactions. In conformity with the equation for the reaction isobar, the equilibrium constants of the polycondensation processes in solution diminish with increasing temperature. From the thermodynamic point of view, it is therefore more convenient to carry them out at a lower temperature, particularly when a weakly basic nucleophile has been selected for their synthesis. The lower limit of the temperature of these reactions is virtually determined by the freezing points of the solutions, which are close to the freezing point of the pure solvent because of the low concentrations of the reactants.

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Polymerisation of *N*-Vinylpyrroles

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Data on the polymerisation of *N*-vinylpyrroles, which have become readily available in recent years as a result of the discovery of their direct synthesis from ketoximes and acetylenes, are described systematically and surveyed. The characteristic features of their radical polymerisation and copolymerisation as well as their copolymerisation with electron-accepting monomers are examined and the mechanism and the unusual nature of the cationic polymerisation processes are discussed.
Attention is concentrated on new examples of the class of *N*-vinylpyrroles, their reactivity, and the structure of the polymers.
The bibliography includes 104 references.

CONTENTS

I. Introduction 609
II. Methods of synthesis of *N*-vinylpyrroles 609
III. Radical polymerisation of *N*-vinylpyrroles 610
IV. Copolymerisation of *N*-vinylpyrroles 612
V. Copolymerisation of *N*-vinylpyrroles with electron-accepting monomers 613
VI. Cationic polymerisation 614
VII. Applications of poly-*N*-vinylpyrroles 615

I. INTRODUCTION

There has been a notable increase of interest in the chemistry of pyrroles in recent years. Two comprehensive monographs[1,2] and a review[3] have been published and the number of journal articles[2] dealing with various aspects of the chemistry of pyrrole derivatives has been increasing continually. This has been stimulated by a number of factors, for example, by the presence in natural objects of various pyrrole derivatives[1,2,4] such as antibiotics, pheromones, and toxins, as well as the discovery of new possibilities for the polymerisation of the pyrrole ring[5,6] and the employment of polypyrroles, which exhibit metal-like electronic conductivity, in the conversion of solar energy.[7-10]

N-Vinylpyrroles can be regarded as extremely interesting monomers for polymerisation and as starting compounds for organic synthesis, with the aid of which it is possible to obtain pyrrole-containing products. However, until recently these were regarded as unavailable and virtually unknown compounds.[1] Beside the evident practical value of poly-*N*-vinylpyrroles (in particular, these are potential semiconductors and photosensitive materials for electrophotography, holography, etc.), their synthesis and study were until recently held back by the difficulty of synthesising the initial monomers. The development of a new general method of synthesis of *N*-vinylpyrroles by the reaction of ketoximes with acetylene,[11,12] for which the name Trofimov reaction has been suggested,[13,14] has now led to virtually unlimited possibilities for the synthesis of monomers of this class.

The characteristic features of the polymerisation of *N*-vinyl monomers have been examined in monographs,[15,16] reviews,[17-20] and dissertations, for example, in Refs.21-23. However, they contain little information about the polymerisation of *N*-vinylpyrroles with the exception of a dissertation[21] in which a large section is devoted to this question. The polymerisation of *N*-vinylindoles has been studied to a much greater extent,[18,24,25] mainly in the systematic investigations of Skvortsova.[26-31]

N-Vinylcarbazole is the most reactive and the most thoroughly investigated monomer of the *N*-vinyl series[15,18] but neither indole nor carbazole are typical pyrroles.

The number of studies on the polymerisation of *N*-vinylcarbazoles which have been published is so large that an adequate survey of these is possible only in an independent review. This review is not therefore concerned with questions of the polymerisation of *N*-vinylcarbazole. It deals with the most significant aspects of certain contradictory features of the polymerisation of *N*-vinylpyrroles and *N*-vinylindoles taking into account the conclusions reached in earlier publications.

II. METHODS OF SYNTHESIS OF *N*-VINYLPYRROLES

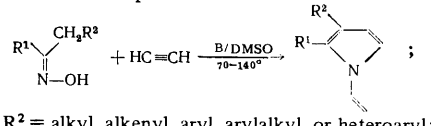
All the methods of synthesis of *N*-vinylpyrroles available until recently were based on the introduction of the vinyl group into compounds containing the pyrrole ring (see Refs.15-18 and the bibliography quoted therein).

NH-Heterocycles are usually vinylated directly with acetylene at elevated temperatures (150-200 °C) and pressures of 15-20 atm in the presence of basic catalysts.[15-18] One of the variants of the vinylation reaction is based on the use of vinyl acetate.[18]

The dehydration of *N*-β-hydroxyethyl derivatives, usually obtained from the corresponding heterocycles and oxiran to give the *N*-vinyl derivatives, takes place in the presence of potassium hydroxide at a reduced pressure and at elevated temperatures.[18]

The elimination of hydrogen halides from *N*-α- and *N*-β-haloethyl derivatives under the influence of bases is also used to synthesise *N*-vinyl monomers.[18]

The method of synthesis of *N*-vinylpyrroles based on the cyclisation of ketoximes with acetylene in a strong base—dimethyl sulphoxide (DMSO)—system has been developing most vigorously. *N*-Vinylpyrroles can be obtained by this reaction, by-passing the pyrroles themselves, from cheap and readily available compounds:[11,12]

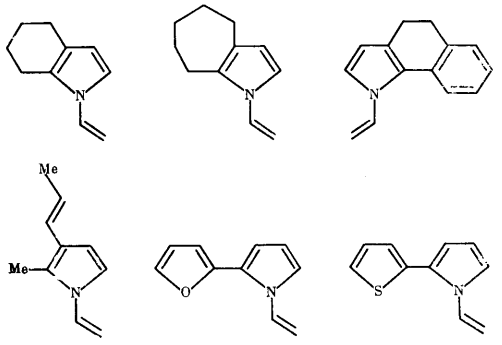


R^1, R^2 = alkyl, alkenyl, aryl, arylalkyl, or heteroaryl;
R^1-R^2 = $(CH_2)_n$, n = 3-5; B = strong base.

The yields of *N*-vinylpyrroles are 70-95% under the optimum conditions.

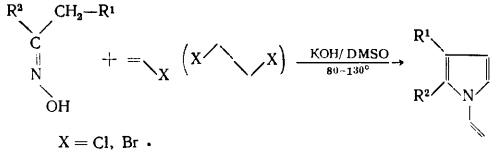
Even *N*-vinylpyrroles in which the initial pyrroles had been difficult to obtain previously by the usual methods or were completely unknown, for example, annelated pyrroles

derived from the oximes of cyclohexanone, suberone, and tetralones, or various alkenyl-, furyl-, and thienyl-pyrroles, became available together with simple alkyl- and aryl-substituted *N*-vinylpyrroles:[12,32-36]



Virtually all ketoximes containing at least one reactive methyl or methylene group in the α-position relative to the oxime functional group undergo this reaction.

A new effective procedure for the direct vinylation of pyrroles in a strong base–DMSO system has been developed.[37,38] *N*-Vinylpyrrole was obtained by this method in high yields under mild conditions at atmospheric pressure and temperatures in the range 80–100 °V (previously NH-heterocycles were vinylated under a pressure of 10–20 atm). Trofimov and co-workers[39-41] showed for the first time that the interaction of ketoximes with vinyl halides or halogenoethane in the same KOH–DMSO system also leads to *N*-vinylpyrroles:



X = Cl, Br .

Depending on the structure of the reactant and the conditions, this reaction can be directed towards the preferential formation of vinylated or non-vinylated pyrroles.[39-41]

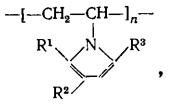
Thus effective, safe, and technologically viable methods of synthesis of *N*-vinylpyrroles, based on the use of cheap and readily available starting materials, namely ketoximes and ultimately ketones and also acetylenes, vinyl halides, and halogenoethane, have now been developed, which creates conditions for their wide-scale employment as monomers.

III. RADICAL POLYMERISATION OF *N*-VINYLPYRROLES

The study of the radical homopolymerisation of a series of *N*-vinylpyrroles has been undertaken.[21,42-44] Its aim was to seek the optimum conditions for the synthesis of the polymers, the analysis of their structure, and also the estimation of the reactivities of the monomers and the properties of the polymers.

It was established beforehand that hydrogen peroxide and benzoyl peroxide do not initiate the polymerisation of *N*-vinylpyrroles, but induce a deep colour in the monomers. It may be that the inertness of hydrogen peroxide under the given conditions is associated with the tendency of *N*-vinylpyrroles, indole, and some of their derivatives to oxidise.[45] The inability of benzoyl peroxide to initiate the polymerisation of certain vinyl monomers is usually explained by the rapid decomposition of the peroxide in the presence of these compounds[46] or by the addition of the products of its decomposition to the monomer, as happens for enamines,[47] ethyl vinyl sulphide,[48] and vinyl ethers.[49]

The homopolymers of substituted *N*-vinylpyrroles having the structure



where R^1 = H, Me, or Ph; R^2 = H or Me; R^3 = H or $COCF_3$; and $R^1 - R^3 = (CH_2)_4$, have been synthesised under conditions of radical initiation by azobisisobutyronitrile (ABIN).[42-44]

The occurrence of polymerisation involving the vinyl double bond has been demonstrated by ^{1}H NMR and infrared spectroscopic data. The absorption bands of the N–CH=CH_2 groups (at 582, 859, 946, 1582, and 1640 cm^{-1}) disappear from the infrared spectra of the polymers, but the characteristic bands of the pyrrole ring remain at 708, 1300, 1490, and 1540 cm^{-1}. The ^{1}H NMR spectra of the polymer contain no signals of the protons of the vinyl group (4.78 and 4.30 p.p.m.) and there are no significant perturbations in the resonance of the protons of the pyrrole rings, although a broadening of the signals characteristic of the polymers is observed.[42-44]

Solutions of the polymers in chloroform and carbon tetrachloride are intensely coloured, which is probably due to the ability of the test compounds to form charge-transfer complexes (CTC) with various halogens, hydrogen halides, and halohydrocarbons, which also happens for *N*-vinylindole[26] and *N*-vinylcarbazole.[20] The possibility of a formation of such complexes has been demonstrated in relation to poly-*N*-vinyl-4,5,6,7-tetrahydroindole.[44] When this polymer has been treated with a hot 1% aqueous HCl solution, its EPR spectrum contains a singlet with a width of 22 G, which can be due to centres of the CTC type (the concentration of unpaired electrons is 3×10^{17} spins g^{-1}). The appearance of a colour on prolonged contact with air justifies the hypothesis of the possible formation of complexes of these polymers with atmospheric oxygen. A freshly prepared polymer is virtually diamagnetic *in vacuo* (10^{-4} mmHg) and contains only traces of a paramagnetic admixture. Heating of the specimen at 150 °C for 5 h does not induce any changes in the EPR spectrum. However, when the polymer has been subjected to an analogous treatment in air after evacuation, its spectrum shows a low-intensity singlet with a width of about 10 g (the concentration of paramagnetic centres is 4.5×10^{16} spins g^{-1}).[44] Consequently the complex is formed precisely with oxygen and is not due to temperature-induced changes in the structure of the polymer leading to an expansion of the conjugation system. CTC of this type are readily decomposed on heating in a high vacuum. The intensity of the EPR signal then falls almost to zero.

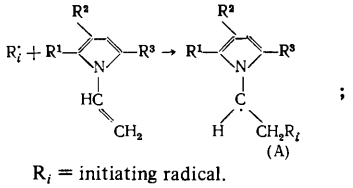
The results of the study of the polymerisation of *N*-vinylpyrroles justify their arrangement in the following sequence in terms of decreasing reactivity: 2-methyl-*N*-vinylpyrrole (I) > *N*-vinyl-4,5,6,7-tetrahydroindole (II) > 2,3-dimethyl-*N*-vinylpyrrole (III) > 2-phenyl-5-trifluoroacetyl-*N*-vinylpyrrole (IV) > 2-phenyl-*N*-vinylpyrrole (V).[42,43]

Conjugation between the pyrrole ring and the N-vinyl group has been demonstrated in *N*-vinylpyrroles by infrared[50] and ultraviolet[51] spectroscopy, NMR,[52,53] and the study of the relative basicities.[54]

According to ^{13}C NMR data,[52,53] the intensity of the $p-\pi$ conjugation in the *N*-vinyl group in the ground state of the series of compounds investigated falls in the sequence (II) ≥ (III) > (I) > (V) > (IV). Consequently the observed sequence of the monomers based on their reactivities in radical polymerisation is not associated directly with the effect of conjugation. Steric factors, namely the decreased probability of collisions with the growing radical and the

steric blocking of the active radical centre for the less compact monomers (III), (IV), and (V), apparently play an important role in the chain propagation stage.

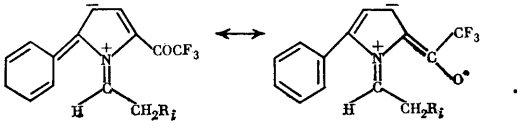
Another important factor influencing the character of the polymerisation should be the relative stability of the radical (A) responsible for chain propagation



(A)

R_i = initiating radical.

The stabilisation and may be the loss of reactivity of the radical (A) owing to the interaction with a neighbouring heteroatomic system will be more pronounced the greater the number of electron-donating substituents or substituents capable of conjugations are present in the ring, which has in fact been observed. Thus the unpaired electron in 2-phenyl-5-trifluoroacetyl-*N*-vinylpyrrole can be effectively distributed via a mechanism involving conjugation with participation of both substituents. For example, one may quote two of the large number of possible canonical structures:



Thus compounds (IV) and (V) should tend to form the most stable and perhaps also the least reactive radical, which in all probability explains their low reactivity in radical polymerisation.[44]

The kinetic parameters of the polymerisation of *N*-vinyl-4,5,6,7-tetrahydroindole have been estimated.[55] It has been established that polymerisation in bulk and in solution in benzene proceeds in the initial stages as a steady-state process at rates which depend on the concentrations of the reactants and the experimental temperature and is described by the equations

$$\lg V_0 = (-3.75 \pm 0.05) + (0.52 \pm 0.02) \lg[I],$$
$$\lg V_0 = (-5.22 \pm 0.02) + (0.98 \pm 0.03) \lg[M],$$

where [I] and [M] are the concentrations of the initiator of the monomer.

The kinetic reaction orders with respect to the monomer and the initiator have been determined together with the effective rate constant for the polymerisation K_{eff}, whose value proved to be virtually identical with K_{eff} for polymerisation in bulk found from the dependence of lg [M] on the reaction time. Thus the initial rate of polymerisation is described by a concentration dependence typical for the polymerisation of vinyl polymers with bimolecular termination of the kinetic chains.

The temperature dependence of the effective rate constant for the polymerisation in bulk is described satisfactorily by the Arrhenius equation

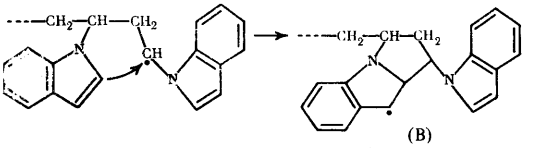
$$\lg K_{eff} = (9.5 \pm 0.4) - (4635 \pm 152) T^{-1}.$$

The effective activation energy and the pre-exponential factor are respectively 88.7 ± 2.9 kJ mol^{-1} and (3.0 ± 1.1) × 10^9 litre$^{1/2}$ $mol^{-1/2}$ s^{-1}. The average rate of initiation is 2.16×10^{-7} mol $litre^{-1}$ s^{-1}.

According to kinetic calculations,[55] the comparatively low chain propagation rate constants in the radical polymerisation of *N*-vinyl-4,5,6,7-tetrahydroindole compared with other vinyl monomers, where the activation energies are approximately the same, are caused by the influence of entropy factors, namely by the steric hindrance induced by the presence of the bulky tetrahydroindole substituents.

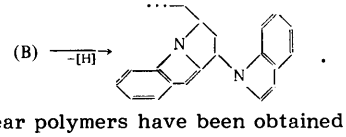
The average length of the kinetic chain ($\bar{\nu}$ = 42–107) greatly exceeds the experimentally observed length of the polymer chain ($\bar{P}$ = 20–33) for the same rate of initiation, which indicates a significant role of transfer processes in the termination of the growing chain. It was demonstrated by special experiments that there is no chain transfer to benzene. Another chain self-transfer constant obtained, which amounts to 1.49×10^{-2}, led to the conclusion that at 60 °C it is impossible to obtain polymers of *N*-vinyl-4,5,6,7-tetrahydroindole with $M_n > 10\,000$.[55]

A possible cause of the oligomeric character of the polymerisation products is intramolecular cyclisation of the macroradical as a result of the attack by the vinyl radical centre on a neighbouring pyrrole ring accompanied by its dearomatisation, the loss of hydrogen, and the subsequent chain transfer to the monomer analogous to that which occurs in the case of *N*-vinylindole:[56]

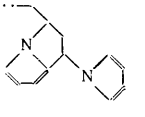


(B)

On the basis of the analysis of the ^{13}C NMR spectra using model compounds, it has been concluded[56] that the radical polymerisation of *N*-vinylindole involves partly the C(2)–C(3) bond of the indole ring and the formation of tricyclic condensed indoline structures, whose content in the polymer is about 25% judging from the intensity of the corresponding ^{13}C signals. Polycyclic radicals of type (B) should evidently exhibit a reduced reactivity as a consequence of stabilisation by the π-electron system and also the enhanced tendency towards chain termination as a result of the abstraction of a hydrogen atom and aromatisation:



The usual linear polymers have been obtained only for the *N*-vinyl derivatives of 2-methyl- and 2,3-dimethylindoles, i.e. compounds in which the 2-position has been substituted. As in the 3-methyl-*N*-vinylindole macromolecules, anomalous indoline structures have been detected in these polymers.[56] On the other hand, there are no anomalous signals in the ^{13}C NMR spectrum of poly-*N*-vinylpyrrole.[56] However, bearing in mind the limited sensitivity of the method, one cannot fully exclude the possibility that the polymer contains (albeit in the form of end fragments) small amounts of the corresponding bicyclic structures:



The formation of additional cyclic structures in the polymerisation of *N*-vinylpyrroles agrees with data obtained in the study of cyclopolymerisation as a phenomenon.[57] Intramolecular cyclisation of this kind can prove to be in a number of instances a thermodynamically more favourable process than intermolecular chain propagation reactions.

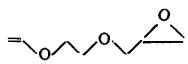
The maximum yield in the radical polymerisation of *N*-vinylindoles reaches 79% (for 2-methyl-*N*-vinylindole), while the minimum yield is 6% (for 2,3-dimethyl-*N*-vinylindole). The molecular weight of the polymers is 4000–10 100.[46]

Thus the reactivity of the monomers and the structure of the polymers formed depend strongly on the positions and numbers of the methyl groups in the pyrrole ring. However, in the series of *N*-vinylpyrroles (I)–(V), it is at present impossible to establish a clear-cut dependence of the reactivity of the monomers on their structure, because the structure is determined not only by different electronic and steric effects but also by the fundamental difference between the chain propagation and chain termination pathways.

IV. COPOLYMERISATION OF *N*-VINYLPYRROLES

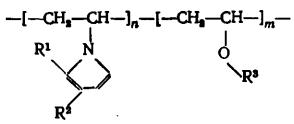
The majority of the known polymers obtained on the basis of monomers with pyrrole rings (mainly as part of the carbazole and indole systems) do not contain functional groups permitting a specific modification of their properties. Interesting possibilities of this kind have arisen from the copolymerisation of *N*-vinylpyrroles with vinyl compounds containing reactive groups such as the oxiran ring.

The copolymerisation of a series of substituted *N*-vinylpyrroles, namely 2-methyl-*N*-vinylpyrrole,[58,59] *N*-vinyl-4,5,6,7-tetrahydroindole,[60,61] and 2-phenyl-*N*-vinylpyrrole[58,59] with the glycidyl vinyl diether of ethylene glycol, called vinylox,[11] has now been investigated:



There are literature data showing that in some cases the copolymerisation of *N*-vinylindole[28] and *N*-vinylcarbazole[20] with various monomers entails the formation of the homopolymers of the initial compounds together with the copolymers. However, the character of the curves for the turbidimetric titration of the copolymerisation products indicates the formation of true copolymers in the given instance.[58,59] This conclusion is supported also by data obtained by fractionating the copolymers in which all the fractions show identical compositions close to that of the initial copolymer.[58,59]

The infrared and ^{1}H NMR spectra of the copolymerisation products confirmed the disappearance of the vinyl groups of the pyrroles and vinylox, the signals of the epoxy-groups in the pyrrole rings remaining unaltered.[58,61] Thus it has been shown that the copolymerisation involves the double bond of the vinyloxy- and *N*-vinyl groups:



R^1 = Me, Ph, $R^1 = R^3 = (CH_2)_4$, $R^3 = (CH_2)_3OCH_2CH{-}CH_2$ (O)

The copolymers are formed for any initial ratios of the monomers and are always enriched in pyrrole units. The initial composition is the main factor which determines the overall rate of reaction and the characteristics of the polymers.

A method for the determination of the content of pyrrole groups in the copolymers from ^{1}H NMR data has been developed in order to estimate quantitatively the composition of the copolymers.[62] The specific activity and polarity factors (see Table) have been determined from the quantitative estimation of the reactivities of *N*-vinylpyrroles within the framework of the *Q*–*l* scheme. The quantities $Q_2 = 0.021$ and $l_2 = -1.44$ for vinylox were used in the calculation.[63] The negative polarity of *N*-vinylpyrroles indicates the electron-donating character of the nitrogen atom in the radical formed. The quantities obtained within the framework of the *Q*–*l* scheme indicate a weaker conjugation (compared with the vinyloxy-group) between the double bond and the heteroatom.

It has been established in the course of partition chromatography that all the copolymers have a unimodal distribution and that their molecular weight is fairly homogeneous.[59]

The "copolymerisation limit", calculated by the method of Prokof'ev et al.[64] for the *N*-vinyltetrahydroindole and vinylox copolymers, is reached when the indole monomer has been consumed, regardless of the composition of the initial mixture, but the degree of conversion is determined by the initial composition.[66]

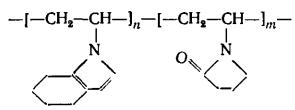
Calculation of the distribution of the copolymer units by the method of Gindin et al.[65] showed that, whatever the initial content of *N*-vinyl-4,5,6,7-tetrahydroindole, large blocks of the given monomer separated by one or two vinylox units predominate in the chain.

The copolymerisation constants (r) and the parameters of the specific activity (Q) and polarity (l) of *N*-vinylpyrroles.[62]

M_1	r_1	r_2	Q_1	l_1
2-Methyl-*N*-vinylpyrrole	6.5	0.05	0.024	−2.86
N-Vinyl-4,5,6,7-tetrahydroindole	5.2	0.06	0.020	−2 45
2-Phenyl-*N*-vinylpyrrole	3.4	0.32	0.013	−1.59

Note. M_1 = *N*-vinylpyrrole and M_2 = vinylox; $Q_2 = 0.21$ and $l_2 = 1.44$.[63]

A method has been developed for the preparation of the copolymers of *N*-vinyl-4,5,6,7-tetrahydroindole with *N*-vinylpyrrolidinone:[44,67]



The copolymerisation was carried out in a solvent or in its absence in the presence of ABIN and the yield of the copolymers reached 66–94%.

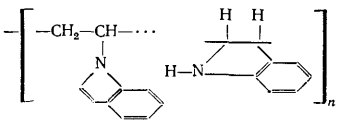
The possibility of using the absorption band of the carbonyl group of *N*-vinylpyrrolidinone at 1690 cm^{-1} for the quantitative determination of the composition of its copolymers was demonstrated previously.[68] The above method has been used also to estimate the composition of *N*-vinyl-4,5,6,7-tetrahydroindole copolymers.[44]

Under the conditions investigated, the maximum content of the tetrahydroindole fragments in the copolymers is 68% and the molecular weight diminishes with increasing fraction of the indole component from 20 000 to 2000. The use of benzene as the solvent reduces the molecular weight of the products without affecting significantly the composition of the copolymers.[44,67,69,70]

Like the *N*-vinyl-4,5,6,7-tetrahydroindole homopolymer, the copolymers are capable of forming complexes of the CTC type with atmospheric oxygen and hydrochloric acid.[44]

Studies[71–73] of the polymerisation of *N*-vinylindole and its 2- and 2,3-methylated analogues established that all the monomers readily polymerise under the influence of free radicals, cationic catalysts, radical-cations, and Ziegler–Natta catalysts and also thermally in the absence of catalysts.

Copolymers with indole, methylindole, indene, and coumarin with equimolar proportions of the monomeric fragments have been obtained under the conditions of thermal initiation:[71–73]



The yield of the polymers is 45% (indole)–78% (coumarin) and the intrinsic viscosity does not exceed 0.2 dl g^{-1}.

The attempts to synthesise the homopolymers of the above comonomers under identical conditions (thermopolymerisation at 150–200 °C) were unsuccessful.[71]

According to gel-chromatographic data, all the copolymers have a unimodal molecular weight distribution.[71] However, the structure of the copolymers has been demonstrated on the basis of infrared spectroscopic data.[71] The intensity of the bands of the indole ring (at 1539 and 714 cm^{-1}) in the infrared spectra of the copolymers is reduced, the band due to the N–H bond (at 3448 cm^{-1}) is present, and the characteristic frequencies of the C=C bond of *N*-vinylindole (at 1612 and 850–820 cm^{-1}) disappear.

The ^1H NMR spectra in deuteriobenzene yield a minimal amount of information as a consequence of the poor solubility of the copolymers but the ratio of the signal intensities of the aromatic and aliphatic protons confirmed the proposed structures.[71]

V. COPOLYMERISATION OF *N*-VINYLPYRROLES WITH ELECTRON-ACCEPTING MONOMERS

The copolymerisation of *N*-vinyl compounds with electron-accepting monomers usually leads to copolymers with a specific structure and properties and also yields interesting information about the formation of charge-transfer complexes and about their role in polymerisation processes. Unfortunately no information about the behaviour of simple *N*-vinylpyrroles in copolymerisation of this kind is as yet available in the literature. It has been stated[74,75] that the copolymerisation of *N*-vinylcarbazole with maleic anhydride is impossible, since the radical-ions formed as a result of the interaction of the monomers induce the kinetically more favourable homopolymerisation of *N*-vinylcarbazole. However, it was later shown that the copolymerisation of these monomers is possible in the presence of free-radical initiators, although some poly-*N*-vinylcarbazole is nevertheless always formed.[76]

A detailed study of the copolymerisation of *N*-vinylindole with maleic anhydride has been published recently.[77] The formation of alternating copolymers of *N*-vinylindole with the acceptor indicated had been published earlier,[51] but no structural characteristics of the products were indicated.

It has also been reported that *N*-vinylindole does not polymerise in acetonitrile at 40 °C in the presence of small amounts of maleic anhydride.[25] On the other hand, under the influence of free-radical initiators, *N*-vinylindole copolymerises with fumaronitrile and diethyl fumarate and the copolymers have a distinct alternating structure.[78–79] As a rule, the monomeric units of the acceptor predominate in the macromolecules of such copolymers as a result of side reactions involving the 3-position of the indole ring.

When *N*-vinylindole and maleic anhydride dissolve in chloroform, a pale-yellow colour appears, which indicates the electronic interaction of the monomers according to the data of Priola et al.[77] However, a distinct upfield shift of the signal of the protons of maleic anhydride is observed in its ^1H NMR spectrum when *N*-vinylindole is added. The shift has been attributed[77] to the reversible complex formation reaction between *N*-vinylindole and maleic anhydride. The equilibrium constant K_e, found[77] by Hanna's method,[80] is 0.25 litre mol^{-1} (in chlorform at 25 °C), which is extremely close to the value K_e = 0.28 litre mol^{-1} obtained for the maleic anhydride–indole system[81] (in chloroform at 20 °C). It is of interest that the same equilibrium constant (0.28) has been found[77] also for the *N*-methylindole–maleic anhydride system. This finding indicates complex formation mainly via the indole ring. Comparison[77] of the data obtained with the values of K_e for the copolymerisation of maleic anhydride with styrene, vinyl acetate, trimethylvinylsilane, ethyl vinyl ether, and ethyl vinyl sulphide leads to the conclusion that the electron-donating properties of *N*-vinylindole and styrene[82] in relation to maleic anhydride are similar and one can therefore expect alternating copolymers with the given acceptor, as for *N*-vinylindole, which is in fact observed in reality. If the copolymerisation is carried out in the absence of an initiator, then thermo- or photo-activation is required for the attainment of an acceptable degree of conversion.[77] Polymers obtained in the presence of free-radical initiators have comparatively high molecular weights (of the order of 56 000).

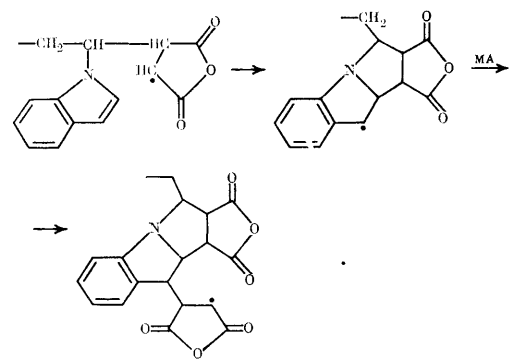
The spontaneous copolymerisation of *N*-vinylindole in the absence of free-radical initiators or Lewis acids suggests that the monomers can form CTC in the initiation stage.

The degree of conversion, the molecular weights, and the composition of the copolymers depend appreciably on the type of solvent in which the copolymerisation is carried out. Highly polar solvents such as acetonitrile or dimethylformamide promote the exclusive formation of the *N*-vinylindole homopolymer. This is explained by the fact that the equilibrium:

$$D + A \rightleftarrows [D \rightarrow A] \rightleftarrows [D^{+\cdot} A^{-\cdot}] \rightleftarrows D^{+\cdot} + A^{-\cdot},$$

where D is the monomer-donor and A the monomer-acceptor, is displaced to the right with increase in the ability of the solvent to solvate the ions.[77]

Analysis of the ^{13}C NMR spectra and the composition of the copolymers led to the conclusion[77] that the copolymerisation is complicated by cyclisation involving the 2-position in the indole ring and additional molecules of maleic anhydride (MA) in accordance with the scheme



The possibility of the participation of the C(2)–C(3) bond of the indole ring in copolymerisation with maleic anhydride has been confirmed by the synthesis of alternating copolymers of unsubstituted indole with the same comonomer-acceptor.[81]

The copolymerisation of maleic anhydride with methylindoles has also been investigated.[77] The fact that the composition of the copolymers does not change significantly as the composition of the initial mixture is varied is regarded as evidence in support of the mechanism of the alternating copolymerisation of *N*-vinylindole and its 2-, 2,3-, and 3-methyl derivatives. It is of interest that 2,3-dimethyl-*N*-vinylindole, for which reactions involving the C(2)–C(3) bond should be difficult, gives rise to 1:1 copolymers. On the

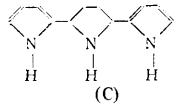
other hand, the dependences of the degree of conversion and of the intrinsic viscosity on the composition of the initial mixture are extremely complex and cannot be interpreted solely on the basis of the idea that the CTC formed undergoes homopolymerisation.

VI. CATIONIC POLYMERISATION

The cationic polymerisation of *N*-vinylpyrroles has been studied to a much lesser extent than the radical polymerisation. If one disregards the vinyl derivatives of carbazole and indole, then there exist apparently only two brief mentions of the polymerisation of pyrroles proper.[17,83] In one of these[83] *N*-vinylpyrrole and vinylindole were mentioned among a large number of vinylamines subjected to polymerisation in the presence of Lewis acids and their complexes with ether such as $ZnCl_2$, BF_3, $BF_3.OEt_2$, $AlBr_3$, $SnCl_4$, and $AlCl(Et_2)$. The polymerisation is carried out without a solvent or in an organic solvent, preferably an aromatic hydrocarbon or ether, in the temperature range from −100° to 100 °C and at a catalyst concentration of 10^{-3} mole per mole of the monomer.

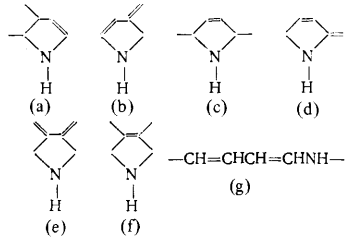
The synthesis of a specimen of poly-*N*-vinylpyrrole by the cationic polymerisation in the presence of $BF_3.OEt_2$, for comparison with the polymer obtained under the influence of an excess of CCl_4 (the polymers proved to be identical according to the infrared spectra), has been described.[25] The conditions of the cationic polymerisation and the yield are not quoted.

In general, bearing in mind the high sensitivity of the pyrrole ring to the action of various acid agents, one can hardly hope for the smooth polymerisation of *N*-vinylpyrroles under the conditions of cationic catalysis. In fact, the pyrroles and oligomers obtained under the influence of strong acids have been known for more than 100 years (quoted after Lamb and Kovachic[84]). In particular pyrrole was trimerised with the aid of HCl as early as 1888. Although different structures were attributed to the trimer formed,[84] only the formula (C), proposed in 1957,[85] satisfies all the available experimental data.

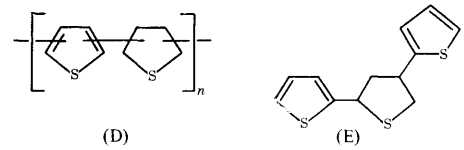


(C)

The polymerisation of pyrrole under the influence of trichloroacetic acid has been studied.[86] However, no data have been presented concerning the structure of the insoluble polymer formed. Later several non-aromatic structures (a)–(g) were proposed for the repeating units of the oligomer chain in the pyrrole oligomer obtained with the aid of the same catalyst:[87]



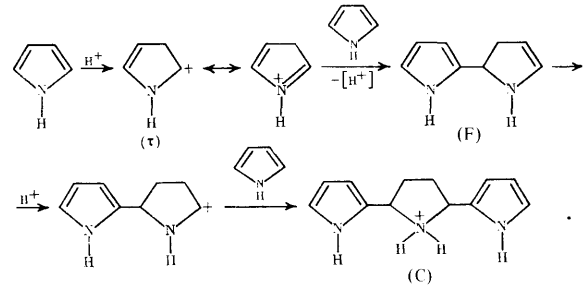
It is known that, on treatment with aluminium chloride or trifluoroacetic acid, thiophen is converted into a polymeric product whose characteristics are closest to formula (B):[88,89]



(D) (E)

The liquid trimer (E) can be obtained by bringing thiophen into contact with phosphoric acid.[90,91] These data as well as the structure of the pyrrole trimer (C) justify the hypothesis that the chain formed in the oligomerisation of pyrrole under cationic conditions has alternating aromatic and non-aromatic structures by analogy with thiophen oligomers.

On the basis of ^{13}C and ^{1}H NMR, infrared and ultraviolet spectroscopic data, the results of mass-spectromatic studies, and the determinations of molecular weights, it has been recently confirmed[84] that the bulk of the pyrrole oligomer obtained in the presence of acids has the trimeric structure (C). The pyrrole ring is known to be protonated mainly in the 2-position.[1,2] This fact gives rise to certain difficulties when attempts are made to account for the formation of the trimer having the structure indicated. In order to obviate such difficulties, it is assumed[85] that, although the 2-protonated pyrrole does in fact predominate in the reaction mixture, its 3-protonated isomer is the more reactive electrophile. Protonation in the 3-position leads to the cation (τ) which in its turn reacts with pyrrole to form the dimer (F). Subsequent attack by its protonated form on the pyrrole ring leads to the protonated trimer (C):[84]



The positive charge on the nitrogen atom of the pyrrolidine ring lowers the reactivity of the neighbouring pyrrole rings with respect to the subsequent electrophilic attack. This is used to explain the relative stability of the trimer compared with other trimerisation products.[85]

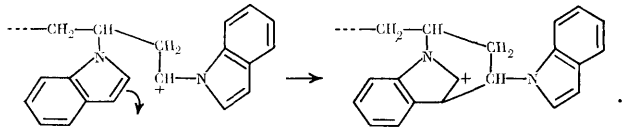
Together with the trimer (A), a coloured insoluble polymer, known for a long time as red pyrrole, is formed when pyrrole is acted upon by strong acids.[84] Its composition is variable, since it is continuously oxidised in air. In terms of its instability, it resembles the trimer. It has been suggested that the formation of "red pyrrole" can entail also ring opening.[84]

The involvement of the pyrrole ring in the formation of the macromolecule has been observed recently in the polymerisation of *N*-vinylindole and its methyl derivatives in the presence of $BF_3.OEt_2$.[56] As in radical polymerisation, the methyl groups in the pyrrole ring influence very significantly the yield, the molecular weight, and the structure of the polymers formed.

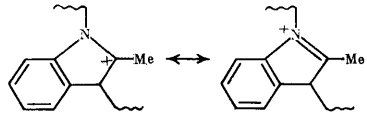
According to ^{13}C NMR spectroscopic data, cyclisation takes place in this case also, although its mechanism differs from that observed in radical polymerisation.[56] The character of the reactivity of the methyl derivatives of *N*-vinylindole is directly opposite to that noted for polymerisation in the presence of radical initiators. Among the methylated *N*-vinylindoles, the 2-methyl derivative gives rise to only

traces of a polymer, while the 3-methyl and 2,3-dimethyl-derivatives are very reactive and readily form polymers with a regular polyvinyl structure and there is no cyclisation side reaction.[56] The polymerisation of unsubstituted *N*-vinylindole leads to products with a partly cyclised structure where the molecular weight and degree of conversion are appreciably lower than for 3-methyl and 2,3-dimethyl derivatives.

It has been suggested[56] that in the cationic polymerisation of *N*-vinylindole the cyclisation reaction proceeds as a result of the attack by the growing cation on the C(3) carbon atom of the indole ring with formation of a six-membered ring in accordance with the following scheme:



The cause of the attack on the 3-position is the high electron density at this carbon atom, typical for indole compounds. All the electrophilic substitution reactions therefore usually proceed precisely in this position.[92] The very low reactivity of 2-methyl-*N*-vinylindole in cationic polymerisation can be explained by the fact that, as a result of intermolecular cyclisation, it forms a more stable tertiary cation, which should therefore be less reactive in the chain propagation stage:[56]



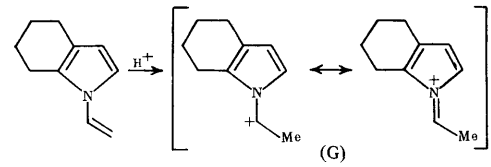
It is well known that, in the presence of halogens, hydrogen halides, alkyl halides, organochlorosilanes, and other electron acceptors, *N*-vinylindole polymerises via the double bond or produces polymeric charge-transfer complexes.[18,26,93,94]

According to Nomori et al.,[25] *N*-vinyl monomers can be arranged in the following sequence in terms of their reactivity towards polymerisation under the influence of electron acceptors: *N*-vinylcarbazole, *N*-vinylindole, *N*-vinylpyrrole. The ionisation potentials of these monomers decrease in the same sequence and hence the ease of their oxidation increases likewise, which is evidently inconsistent with the initiation mechanism postulating electron transfer as the key stage. At the same time, electron acceptors can be arranged in the following sequence in terms of their reactivity in polymerisation: dichlorodicyanobenzoquinone > *p*-chloranil > dichloro-*p*-benzoquinone > tetracyanoethylene > maleic anhydride. This sequence of electron acceptors is consistent with the sequence of the electron affinities and hence with the proposed polymerisation mechanism.

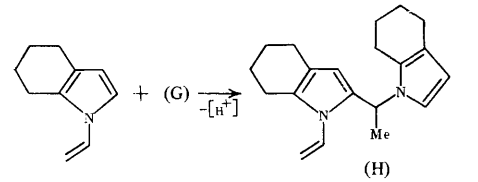
An *N*-vinylpyrrole polymer has been obtained in the presence of excess CCl_4 and the infrared spectrum of the product was consistent with the spectrum of the poly-*N*-vinylpyrrole synthesised in the presence of boron trifluoride etherate.[25]

It must be emphasised that the mechanism of polymerisation in the presence of carbon tetrachloride is not regarded as ultimately elucidated even for *N*-vinylcarbazole, despite the large number of studies devoted to this question.[20]

When *N*-vinyl-4,5,6,7-tetrahydroindole was acted upon by hydrochloric acid, a dimer, the product of electrophilic attack by the immonium cation on the pyrrole ring, was obtained together with the polymer:[95]



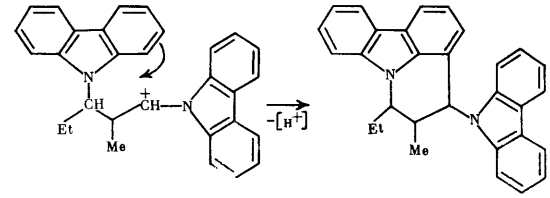
(G)



(H)

When hydrochloric acid is replaced by chlorotrimethylsilane, the yield of the dimer increases to 70%. This reaction leads to interesting possibilities for the synthesis of new *N*-vinylpyrroles.

Even the benzene fragments of the carbazole ring can be subjected to intramolecular attack by the growing cation. This has been demonstrated[22] for *N*-alkenylcarbazoles, which do not form high-molecular-weight products under the influence of acids (H_2SO_4 and $BF_3.OEt_2$), the main reaction being dimerisation. Thus the dimer of *N*-*trans*-propenylcarbazole gives rise to a cyclic product having the following structure:



VII. APPLICATIONS OF POLY-*N*-VINYLPYRROLES

Until recently, *N*-vinylcarbazole was the only widely available representative of the series of *N*-vinylpyrroles. A whole series of promising applications of this polymer have already been discovered: as insulating materials for the electrotechnical industry, particularly in high-frequency technology, and as components for the modification of synthetic rubbers.[15]

Poly-*N*-vinylcarbazole is one of the first and most vigorously investigated photosensitive polymeric systems, the interest in which is due primarily to their possible technological application in non-silver image recording processes—electrophotography, photothermoplastic recording, etc.[96,97]

The stream of publications on the properties and applications of *N*-vinylcarbazole is so great (see, for example, the relevant reviews[96-99]) that the problem indicated apparently requires special consideration and will not therefore be analysed in this article.

A photoconducting polymeric material has been obtained from the copolymers of *N*-vinylindole and its 2- and 3-methyl derivatives with *N*-vinylcarbazole or styrene.[72] These copolymers could be used as solutions or melts forming photosensitive layers for electrophotography.

The thermal copolymerisation of *N*-vinylindole with indole or other heterocyclic compounds having an endocyclic double bond leads to copolymers containing 2,3-indoline fragments in the main chain and indole rings in the side chain.[71-73] These polymers can also be used in electrophotography.

Poly-*N*-vinylpyrroles with high melting points have been synthesised in liquid SO_2 at −10° to −70 °C.[100]

Polyvinylindole has been investigated as a catalyst of photochemical polymerisation using its ability to form radical-ions.[101]

Polymers of *N*-vinylpyrroles having a stable colour have been described in patents.[102,103] The copolymers of *N*-vinyl-4,5,6,7-tetrahydroindole with vinylox sensitised by trinitrofluorenone are photosensitive and are capable of being hardened by polyamines like the usual epoxyresins.[61,66]

The study of the thermal stability of these copolymers by differential thermal analysis demonstrated the possibility of extending the temperature range of the use of the copolymers by introducing the indole component.[60]

In order to increase the assortment of reactive polymeric materials for the synthesis of medicinal drugs, a method has been developed for the preparation of the copolymers of *N*-vinyl-4,5,6,7-tetrahydroindole with *N*-vinylpyrrolidinone.[44,67] Water-soluble copolymers enriched in *N*-vinylpyrrolidinone exhibit an antisilicosis activity in model pneumoconiotic processes,[70] while the *N*-vinylpyrrolidinone homopolymer does not show such an activity.[104]

Products based on annelated pyrroles have been employed for the enrichment of polymetallic ores by flotation.[69] The polymeric flotation agent exhibits effective foam-producing properties when employed in amounts as low as 10 g per tonne of ore and the overall extraction of zinc and lead under these conditions reaches 175% [sic., Ed.], while under analogous conditions industrial foaming agents extract only 90% of the metals.[69]

Overall, the chemistry of *N*-vinylpyrroles is too new to compete successfully as regards practical applications with the chemistry of other pyrroles and even with that of *N*-vinylcarbazole. The examples quoted illustrate only the first advances achieved in the applied employment of *N*-vinylpyrroles.

Thus it follows from the literature data quoted that the chemistry of *N*-vinylpyrroles is developing very vigorously. At the same time some of its aspects have only been outlined for possible investigation. These include the cationic polymerisation whose key stage is the electrophilic substitution of hydrogen in the pyrrole ring by the immonium cation. This reaction can lead to new condensed polycyclic systems.

A characteristic feature of the present state of the chemistry of *N*-vinylpyrroles is the virtually complete absence of quantitative data concerning the polymerisation process and hence the absence of a clear-cut correlation between the structure of the monomers and their reactivity.

In the next few years one may expect the synthesis of new polyvinylpyrroles with properties of practical value both as a result of the use of new monomers of this series and as a result of the chemical modification of the highly reactive pyrrole ring in the polymers already known.

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Reactions in Organic Crystals

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Structural investigations of two types of chemical reactions occurring in organic crystals on heating and irradiation are examined, namely intermolecular rearrangements (including the rearrangement of molecules via the transfer of individual atoms and groups of atoms, isomerisation, stereo-isomerisation, etc.) and reactions with elimination of small molecules (N_2, CO_2, H_2O, HHal). Solid-phase processes are discussed in terms of topochemical reactions and reactions in non-crystalline (amorphous) regions.
The bibliography includes 195 references.

CONTENTS

I. Introduction 619
II. Intermolecular rearrangements 621
III. Reactions with elimination of small molecules 634

I. INTRODUCTION

Reactions occurring in the solid phase have been known for a long time but they have attracted increasing attention recently, because of two main factors. The first of these is that the occurrence of reactions in the solid phase imposes significant limitations on the mobility of the reacting molecules. This not only facilitates the experimental and theoretical study of chemical reactions in the crystal but frequently creates completely new (compared with traditional liquid-phase reactions) possibilities for their investigation. The combined use of various techniques for the investigation of solid-phase reactions makes it possible to follow the entire chain of molecular transformations taking place and in a number of instances to achieve a well-founded characterisation of their mechanism. The first advances on these lines have already been made as regards the mechanisms of intramolecular rearrangements, reactions with elimination of small molecules, etc. The second factor is that the practical use of the possibilities of solid-phase synthesis which cannot be achieved in liquid- or gas-phase reactions (for example, the preparation of crystalline polymers with chains having a regular structure, the formation of enantiomerically pure products with the configuration of asymmetric centres specified beforehand, etc.) was initiated in recent years.

It is possible to differentiate two main types of solid-phase reactions: topochemical reactions and reactions in non-crystalline regions.[1,2]† The topochemical character of the

†Topochemical reactions consist in the conversion of the molecules of the initial substance into those of the product without the disturbance of the crystal lattice and without the formation of non-crystalline intermediates.[1-4] The relation between the crystallographic directions of the product of the solid-phase process and the initial substance is then referred to as topotaxy.[1]

process makes it possible to predict the structure of the product formed, which is by no means possible in all non-topochemical reactions.

The essential condition for the occurrence of intermolecular solid-phase topochemical reactions is that the shifts in the equilibrium positions of the atoms in the interacting molecules are small, while the thermal vibrations of the molecules themselves are fairly strong. This general principle, formulated by Schmidt,[5-7] can be specified in a more concrete form for solid-phase reactions of the most varied types. For example, it has been established empirically that, in the photochemical interaction of unsaturated molecules in the crystal via their C=C π bonds, topochemical control requires that these bonds should be oriented in parallel and that the atoms formed should be separated from one another by not more than 4.0 Å.[8] In order to stimulate chemical reactions in the solid phase, one employs nowadays virtually all the procedures for the usual chemical reactions, but it is entirely clear that the maximum topochemical control is possible when the solid-phase reactions are carried out with photoirradiation, which makes it possible to create the optimum conditions for the realisation of the principle indicated above. Schmidt's principle has been somewhat modified.[9] The preferred reaction in the crystal is that which requires the minimum change in the form of the "reaction cavity" (the space incorporating the reacting molecule before the reaction and the molecule of the reaction product). The principle of the conservation of the shape of the reaction cavity is especially useful for the explanation of chemical reactions in clathrates and for the description of the reactivities of excimers in crystals.

It must be emphasised that topochemical factors operate also in solid-phase intramolecular reactions, creating in this instance a kind of external limitation to the atomic shift necessary for the occurrence of the reaction (when the internal limitations are defined as those caused by the structure of the molecule itself).[10]

A disposition of the molecules suitable for the reaction is sometimes not inherent in the periodic lattice of the crystal but arises only when defects or dislocations are formed in the latter. However, in this instance too, as in topochemical reactions, the process actually occurs under the control of the lattice, since its direction and mechanism are determined by the fixed disposition of the interacting molecules.

The most important method for the investigation of solid-phase reactions is X-ray diffraction analysis, since it enables one to establish vigorously and quantitatively all the structural and geometrical parameters of the starting materials and final products (the valence and dihedral angles and the bond lengths), so that the process occurring can be adequately characterised when a topochemical mechanism operates. Under the conditions of a non-topochemical mechanism, information about the defects and dislocations and about their number and the principal reaction pathways can be obtained with the aid of electron microscopy. However, this is insufficient for the establishment of the orientation of the molecules at the dislocation boundaries. Computational methods, whereby one can model both the character of the relative disposition of the molecules and the possibility of their displacements in the course of a reaction, are frequently employed in such instances.

An important characteristic of solid-phase processes is their homogeneity or heterogeneity. By a homogeneous process one understands in this instance one whose product forms a solid solution in the lattice of the initial compound. In the corresponding heterogeneous process the product forms its own lattice and does not give rise to solid solutions in the initial compound. In a homogeneous mechanism a transition of the single crystal → single crystal type takes place, while in a heterogeneous mechanism the single crystal of the initial compound disintegrates. One must note that in a number of instances solid-phase reactions are investigated in polycrystalline specimens, which hinders their X-ray diffraction study. Since data concerning the structure of the crystal obtained from an X-ray diffraction study are averaged both in space (throughout the crystal) and in time, it is difficult to characterise by this method the homogeneity and heterogeneity of the process (with the exception of cases of the so-called dynamic X-ray diffraction analysis used for comparatively slow processes). Important additional information about the character of solid-phase processes and about the movement of the molecules involved in the reaction can be obtained from Raman phonon spectra. Thus a sufficiently complete picture of solid-phase processes can be obtained solely by a combined study of the structure and reactivity of the organic crystals using the entire set of the methods indicated above.

Investigation of chemical reactions in solid crystals (see the relevant reviews[1,9-17]) led to the development of a new scientific discipline, which arose recently at the frontier between organic chemistry and organic crystal chemistry (crystal engineering). The aim of this new discipline is to understand and formulate the main rules and principles governing the structure of the packing of potentially reactive molecules in crystals such that the most favourable conditions are created for the participation of the molecules in particular chemical reactions and rearrangements without the need for diffusion and requiring only a slight rearrangement of the crystal packing with topochemical control of the process.[17]

This paper represents a review of the structural investigations of chemical reactions in organic crystals published mainly after the appearance in 1977 of our previous review on this topic.[1] The review includes various types of thermal and photochemical intramolecular rearrangements and reactions involving the elimination of small molecules in crystals of organic compounds. In order to demonstrate the wide-scale occurrence of solid-phase reactions, several types of solid-phase processes in molecular crystals formed by complex compounds have also been examined.

The proposed subdivision of the reactions considered in the review into intramolecular rearrangements and reactions involving the elimination of small molecules is to some extent arbitrary. The first of the above two types includes processes in which the overall composition of the molecules of the initial substances and final products is the same. The character of the rearrangements taking place under these conditions is fairly varied. They can be intramolecular, whereupon only proton transfer can lead to a significantly different result: for example, it can lead to a significant alteration of the molecular skeleton, which entails a change in the chemical properties of the compound or to insignificant geometrical changes (the transfer of a hydrogen atom via a hydrogen bond and small conformational changes), as a consequence of which a significant alteration of the physical characteristics of the specimen, particularly its colour, takes place.

The rearrangements of molecules can also take place via the transfer of larger atomic fragments, in particular, methyl or phenyl groups. Together with the instances of intramolecular mechanism, such as, for example, that operating in the stereoisomerisation of metal complexes, there is also a possibility in this case of intermolecular processes. It must be emphasised that all the processes involving the transfer of atoms or groups of atoms mentioned above take place in the manner stated only by virtue of their suitable disposition in the crystal and such disposition can be both inherent in the structure of the crystal itself and can be "created" at its defects or dislocations.

The character of reactions of the second type (with elimination of small molecules) is in most cases predetermined not only by the very disposition of the molecules but also by their interactions in the crystal, in particular, by the existence of a system of intermolecular hydrogen bonds whose chains provide a pathway for the reaction. A striking manifestation of the role of such interactions is provided by the differences between the reactions on different faces and along different directions in crystals.

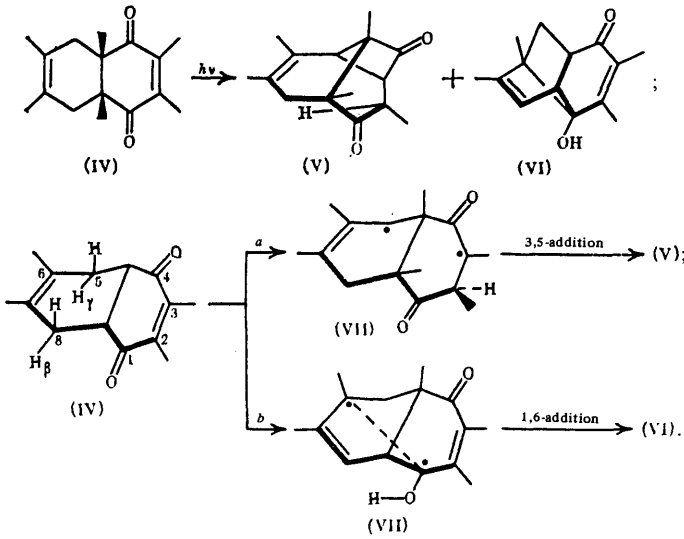
II. INTERMOLECULAR REARRANGEMENTS

The study of the controlling influence of molecular packing in the crystal and the photochemical behaviour of organic systems undergoing unimolecular photo-rearrangements in solution was initiated, according to Scheffer,[10] by investigations of the photoreactions of santonin (I) in the solid phase. It was observed that the photolysis of crystalline santonin results in the formation of a product whose appearance can be accounted for by the formation and subsequent dimerisation of cyclopentadienone (III) and not of luminosanton (II), as in solution (scheme 1). However, the relation between the structure and reactivity remained unelucidated in this instance and required further study.

1. Isomerisation of Naphthoquinone Derivatives

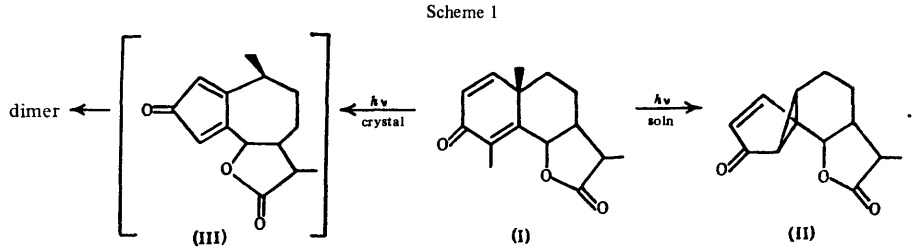
Studies of the photochemical reactions of solutions of Diels-Alder adducts of non-cyclic 1,3-dienes with *p*-quinones have shown that two main types of reactions, which depend on the character of the substituents in the initial adduct, are characteristic of these systems.[18,19] The interaction of a quinone and 1,3-dienes [for example, of the 2,3-dimethylbutadiene adduct (IV) (Scheme 2)] on irradiation of the solution, leads to the formation of cyclobutanones of type (V) as the main product, while compound (VI) has been detected as the side product [with the ratio (V):(VI) = 2:1]. The formation of these photoproducts requires at first sight a very major molecular rearrangement of compound (IV), but it was found that irradiation of crystals of compound (IV) yields the same products and in the same proportions (2:1) as in solution.[20,21]

Scheme 2



The cyclohexane ring of the molecule of compound (IV) has the half-chair conformation in the crystal and has a *cis*-junction with the approximately planar enedione ring. The formation of cyclobutanone (V) (reactions *a* in Scheme 2) takes place as a result of the transfer of the allyl hydrogen atom H_γ to the C(2) atom of the enedione chromophore and the subsequent formation of a bond between the C(3) and C(5) atoms in the biradical (VII) produced. The mechanism of the formation of the dienol (VI) (reaction *b* in Scheme 2) should include the initial excitation of the molecule with subsequent transfer of the H_β atom to the O atom of the carbonyl group at C(1) with formation of the intermediate biradical (VIII). The occurrence of these two competing solid-phase

Scheme 1



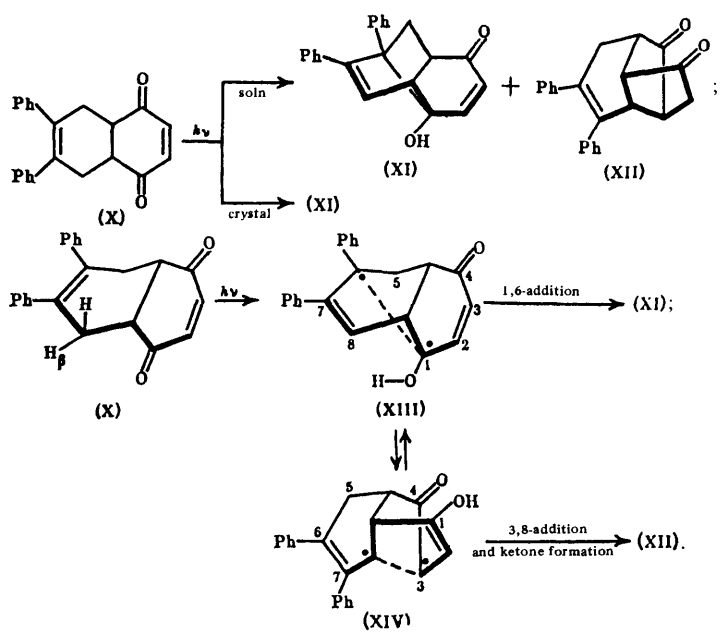
photoprocesses is determined by two factors: (1) the geometry of the initial molecules is extremely favourable for intramolecular transfers of hydrogen atoms; (2) the intermediate states arising in the transfer of H atoms are ideally suitable for the subsequent intramolecular interaction of the biradicals produced. The form of the molecules of the photo-products (V) and (VI) is then extremely similar to that of the initial molecule of compound (IV).[6] Analogous data have also been obtained for the adducts produced in the Diels-Alder reaction between duroquinone and *trans,trans*-hexa-2,4-diene (IX).[10]

Photolysis of the Diels-Alder adduct of *p*-benzoquinone with 2,3-diphenylbutadiene (X) in solution affords the products (XI) and (XII) in proportions of 3:1 (Scheme 3);[10] in this case photoproducts of the type of cyclobutanone are not formed. Photolysis of compound (X) in the solid phase leads to the unsaturated alcohol (XI), which can be regarded as an analogue of compound (VI); the diketone (XII) is not formed. An answer to the question of the causes of the differences between the reaction products in different media was provided by an X-ray diffraction study of compound (X).[22] Since the overall twist-conformation of the molecule of compound (X) found in the crystal apparently predominates also in solution, presumably the reaction in both liquid and solid phases begins with the same conformation as that of the initial molecule of compound (X) and the differences between the reaction products are determined by the conformational flexibility of the biradical intermediate (XIII) produced when a β-hydrogen atom is transferred. In fact the biradical (XIII) has the same conformation as its precursor (X) and can undergo biradical condensation to the dienone alcohol (XI) both in solution and in the solid phase. The direct formation of the diketone (XII) and the biradical (XIII) is sterically impossible[10] and requires a conformational rearrangement of the rings with transition to the biradical (XIV). Naturally, such a transition, which is permissible in solution, is no longer possible in a crystal, so that the photoproduct (XII) is formed only when the reaction is carried out in the liquid phase.

Another example of the different course of a chemical reaction in the crystal and in solution, due to the different possibilities for the necessary conformational rearrangements of the reacting molecules in the liquid and solid phases, is provided by the intramolecular rearrangement in the crystals of 1,3-diphenylindan-2-dione and *NN*-dialkyl-α-oxoamide.[23,24] If the molecular structure limits the possible conformational rearrangements, then the reaction products in solution and in the crystal are as a rule identical; for example, the presence of the axial CH_3 group in the molecule of compound (IV) prevents the rearrangement of the intermediates (VII) and (VIII) and leads to identical products of the photochemical reaction of compound (IV) in both phases investigated.

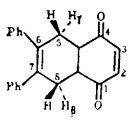
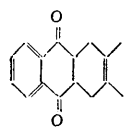
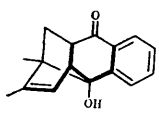
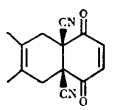
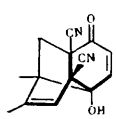
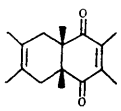
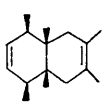
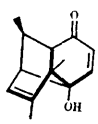
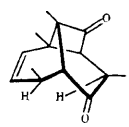
All the photochemical reactions considered begin with the intramolecular abstraction of a hydrogen atom. Table 1 presents data for the geometry of five compounds, in which photoinitiated solid phase abstraction of a β-hydrogen atom by the carbonyl oxygen atom (leading to the formation of an enone alcohol) has been observed, as well as two adducts produced by the Diels-Alder reaction in which a γ-hydrogen atom is abstracted by the enone carbon atom with formation of photoproducts of the cyclobutane type. Although the data in Table 1 do not refer to the real geometry of the molecule at the instant of photochemical reaction (X-ray diffraction study has yielded the parameters for only the ground electronic state), they nevertheless can reveal the factors which favour such reactions. This applies particularly to the transfer of a β-hydrogen atom to oxygen, since it is quite likely[25-32] that the carbonyl fragment in enones (and apparently also in enediones) retains the geometry of

Scheme 3



its ground state on photochemical excitation. Even when a H_β atom is transferred to the enone C atom, the X-ray diffraction data for the relative positions of the H_γ and C(2) atoms reproduce fairly exactly the geometry of the excited state, because the twisting of the enone C=C π-bond on formation of the activated state alters mainly the parameter τ_C [25-32] (data concerning the possible planarity of the enone molecules in the activated state are quoted by Dyxtra[33] and Jones and Kearns[34]). We may note that such twisting can facilitate the abstraction as a result of the more exact alignment of the 2p orbital of the C(2) atom with the direction of the H_γ atom, i.e. as a result of the increase of the angle τ_C in the direction of the ideal value of 90°.[10]

Table 1. Intramolecular solid-phase reactions accompanied by the transfer of a hydrogen atom.[15]

Initial compound	Product containing the enone fragment	$R(H_\beta...O(1))$, Å	τ_O, deg	Δ_O, deg	Product containing the enedione fragment*	$R(H_\gamma...C(2))$, Å	τ_C, deg	Δ_C, deg
	(XI)	2.46	3	81.3	*	—	—	—
		2.57	5	80.7	*	—	—	—
		2.58	8	83.6	*	—	—	—
	(VI)	2.47	0	85.1	(V)	2.89	52	72.6
		2.26	1	86.4		2.66	50	74.4

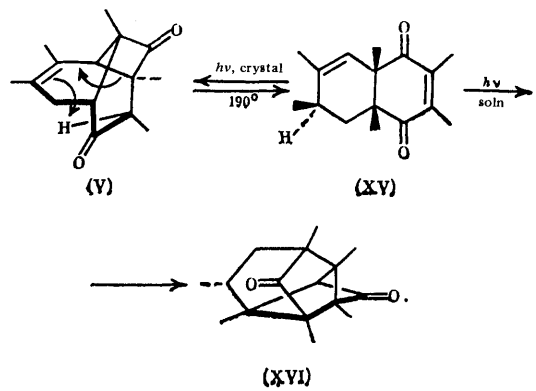
Notation: τ_O is the deviation of the H_β atom from the plane of the carbonyl group at the C(1) atom, Δ_O is the angle $C(1)O(1)H_\beta$, τ_C is the deviation of the H_γ atom from the plane of the C(2)=C(3) double bond, and Δ_C is the angle $C(3)C(2)H_\gamma$.

*Does not form.

The distances between the hydrogen atom and the "abstracting" atom over which the transfer of a hydrogen atom is observed vary from 2.26 to 2.58 Å for abstraction by oxygen and from 2.66 to 2.89 Å for abstraction by carbon, which agrees with the difference between the van der Waals radii of the oxygen and carbon atoms (1.52 and 1.70 Å).[35,36] It is believed[10] that the intramolecular transfer of a hydrogen atom is feasible over distances comparable to the sum of the van der Waals radii of the interacting atoms. If one begins with the postulate that the radius of the hydrogen atom is 1.20 Å,[36] these sums are 2.72 Å for the H and O atoms and 2.90 Å for the H and C atoms. These values are appreciably higher than those proposed earlier on the basis of calculations and/or molecular models. For example, a spherical "activated volume" of the carbonyl group, whose radius has been estimated as 1.7–2.1 Å, has been proposed[37] for the intramolecular photochemical hydrogen atom transfer reactions.

The relative orientation of the orbitals of the "abstracting" atom and the hydrogen atom is no less important. Table 1 shows that the β-hydrogen atom is located in all cases (within the limits of several degrees) in the mean-square plane of the "abstracting" carbonyl group, which favours the thoroughly investigated[38] transfer of a hydrogen atom to the excited carbonyl fragment located in the same plane. The values of Δ_O for these systems are close to 90° (Table 1) and are almost ideal for the transfer considered.[10]

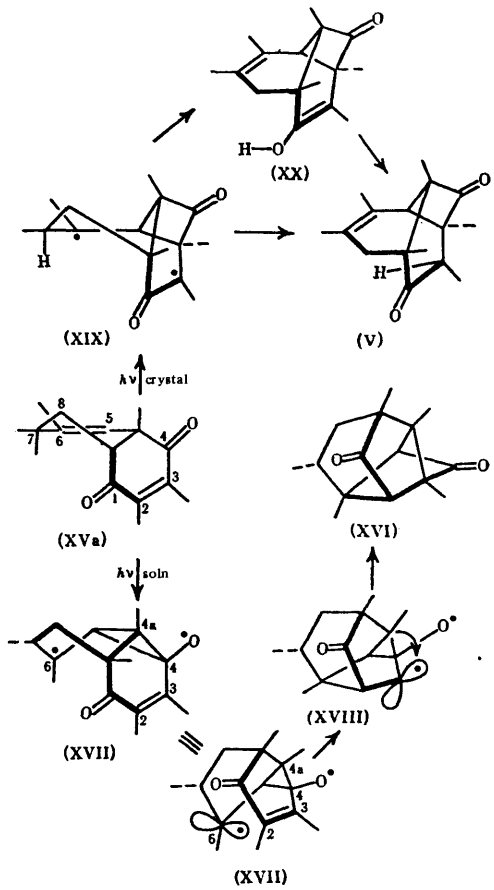
Scheme 4



In the course of thermolysis at 190 °C cyclobutanone undergoes the retroene reaction (Scheme 4), giving a satisfactory yield of the crystalline β,γ-unsaturated ketone (XV),[18] whose further photochemical reactions in solution and in the crystal proceed in entirely different ways. Whereas the explosive photoproduct (XVI) is formed in solution, the initial cyclobutanone (V) is regenerated almost quantitatively in the crystal.[39] According to X-ray diffraction data, the ketone (XV) has the conformation (XVa) in the crystal (Scheme 5) and the bulky CH_3 substituent at the C(7) atom occupies a pseudoequatorial position in this instance. If it is assumed that compound (XVa) behaves as a typical $^3(\pi,\pi^*)$-excited βγ-unsaturated ketone, then in the first stage it should undergo the well known oxadi-π-methane rearrangement[40-43] consisting in the formation of a bridge between the carbonyl carbon atom and the vinyl group, which leads to the product (XVII). The transition to compound

(XVI) requires then the rupture of the C(4)–C(4a) bond with formation of the C(4a)–C(3) and C(6)–C(2) bonds (Scheme 5).

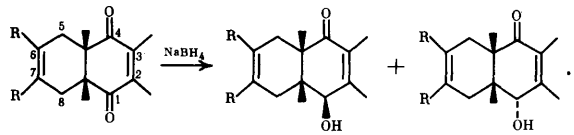
Scheme 5



It has been noted[10] that each stage of the transition (XV) → (XVI) involves a significant displacement of the atoms and deformation of the molecule and leads ultimately to a product, the form of the molecule of which has very little in common with that of the initial molecule. This is not observed in the solid-phase rearrangement, which constitutes a radical difference between the reactivities of compound (XV) in the two different phase states examined.

A detailed comparison has shown that the molecular shapes of compound (XV) and of its photoproduct (V) are very similar. Compound (V) is formed as a result of the appearance of the C(3)–C(5) bond [the 2*p* orbitals of the C(3) and C(5) atoms are directed towards one another; the C(3)...C(5) distance is 3.12 Å, which is less than twice the van der Waals radius of the C atom (3.40 Å)[20]] via the intermediate compound (XIX), which is followed by the intramolecular transfer of the pseudoaxial hydrogen atom from the C(7) atom to the C(2) atom, which takes place either directly or via the enol (XX). The configuration of the C(7) atom in compound (XVa) is extremely favourable for such transfer: the H(7)...O(1) distance is 2.64 Å and we have the angles $\tau_C = 28.5°$ and $\Delta_O = 84.7°$. The mechanism of the solid-phase transition described requires a minimum displacement of the atoms from the initial positions: the C(2), C(3), C(5), and C(7) atoms are rehybridised and the C(3) and C(5) atoms approach one another, but the overall molecular shape is retained. Another mechanism of the (XV) → (V) transformation, differing from the foregoing by the sequence of stages, has also been proposed.[15]

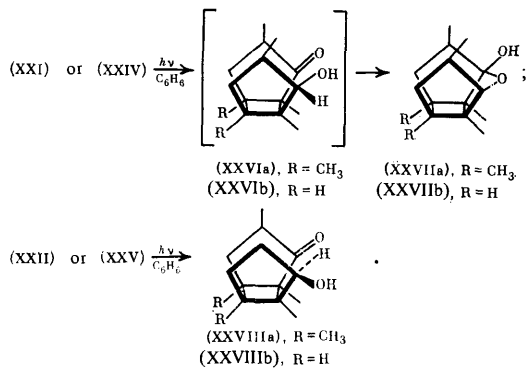
Scheme 6



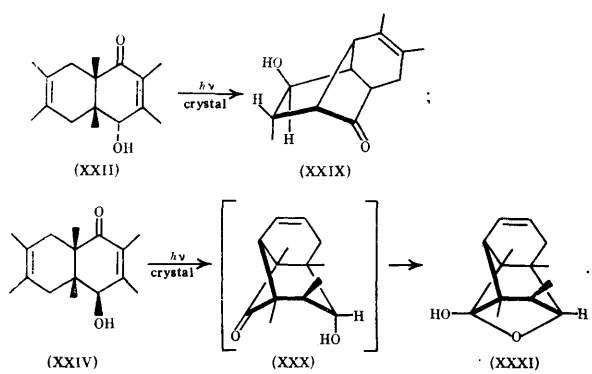
(IV), R = CH_3 (XXI), R = CH_3 (XXII), R = CH_3
(XXIII), R = H (XXIV), R = H (XXV), R = H

The reduction of the duroquinone–butadiene Diels-Alder adduct (IV) leads to a mixture of the alcohols (XXI) (50%) and (XXII) (35%) (Scheme 6). Analogously, the reduction of the duroquinone–butadiene adduct (XXIII) affords the products (XXIV) (63%) and (XXV) (31%). The photochemical behaviour of these products in the solid phase differs sharply from that observed in solution.[44,45] Irradiation at $\lambda > 330$ nm of benzene solutions of all four tetrahydronaphthoquinones (Scheme 7) leads to products of the intramolecular [2 + 2]-cycloaddition having the tetracyclo[5.3.0.$0^{2,6}$.$0^{4,9}$] decane skeleton. In compounds (XXI) and (XXIV) the configuration of the carbon atom to which the OH group is attached is such that the ketoalcohols (XXVIa) and (XXVIb) formed initially cyclise to the internal hemiacetals (XXVIIa) and (XXVIIb). At the same time the formation of similar acetals from the photoproducts (XXVIIIa) and (XXVIIIb) is not observed.

Scheme 7



Scheme 8

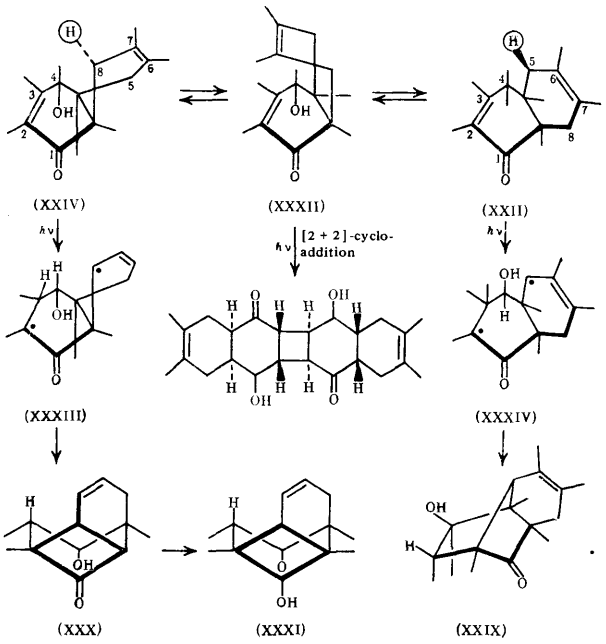


Irradiation of the same substances in the solid phase does not lead to the formation of products with a skeletal structure. The character of the photoproducts formed in the

solid phase is determined, as in solution, by the disposition of the hydroxy-groups in the substrate molecule; a typical picture is presented in Scheme 8. We may note that irradiation of the polycrystalline specimens of compound (XXII) is used to obtain the ketoalcohol (XXIX); the photolysis of the polycrystalline compound (XXIV) is used in exactly the same way for the quantitative formation of the hemiacetals (XXXI) (a structural scheme for this process has been published[31]).

Scheme 9 illustrates the conformation of the molecules of the cyclohexenones (XXII) and (XXIV) in the crystal;[46] the cyclohexenone ring in the half-chair conformation has a *cis*-junction with the cyclohexene fragment (also in the half-chair conformation). Since the carbon atoms attached to the OH substituents have the opposite configurations in compounds (XXII) and (XXIV), these molecules are characterised by the opposite directions of the twist of the second ring. The photoproduct (XXXI) is formed from the conformer (XXIV) as a result of the transfer of the allyl hydrogen atom from C(8) to C(3) and the subsequent formation of the C(2)–C(8) bond in the biradical (XXXIII). The photoproduct (XXIX) is formed via the conformer (XXII) as a result of the C(5) → C(3) transfer of the allyl hydrogen atom and subsequent formation of the C(2)–C(5) bond in the biradical (XXXIV) produced.

Scheme 9



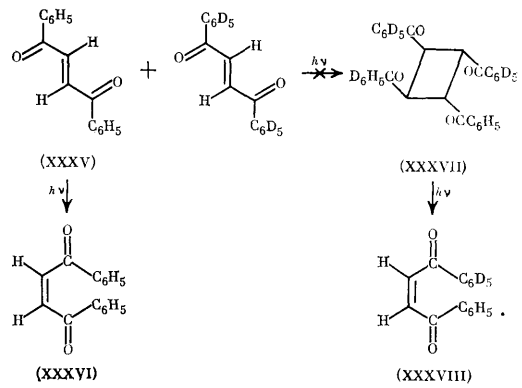
As in the other cases described above, the reactions of compounds (XXII) and (XXIV) proceed with minimal deformations of the molecules. The transfer of a hydrogen atom is achieved over a distance of 2.72 Å in compound (XXII) and 2.84 Å in compound (XXIV), which is less than the limiting distance of 2.90 Å required for the transfer to a carbon atom. The conformational similarity of the biradicals (XXXIII) and (XXXIV) with the products (XXXI) and (XXIX) is also significant.

Comparative analysis of the reactivities of the isomers (XXI) and XXII) in the solid phase, carried out on the basis of their X-ray diffraction study,[47] has shown that the molecules have different conformations in the crystal and the distances from the H_γ atoms to the C(2) and C(3) atoms in compound (XXII) are somewhat smaller than in compound (XXI) (2.78 and 2.72 Å in the former case and 2.88 and 2.92 Å in the latter), which accounts for the reactivity of compound (XXII) [and the lack of reactivity of compound (XXI)] in a solid-phase reaction proceeding via the transfer of a H_γ atom to the β-enone C(3) atom. We may note that the angles Δ_C and τ_C (Table 1) in compounds (XXI) and (XXII) proved to be similar: 75.2° and 78.5° in the former case and 49.3° and 53.2° in the latter.

2. Isomerisation of 1,2-Dibenzoylethylene

Crystalline *trans*-1,2-dibenzoylethylene (XXXV) is gradually converted into the *cis*-isomer (XXXVI) in the light.[48] Since the corresponding cross-product, namely benzoyl(pentadeuteriobenzoyl)ethylene (XXXVIII), was not detected by the mass spectrometry of a solid solution of the bispentadeuteriated analogue of compound (XXXV) and the non-deuteriated compound (XXXV) was used in this reaction, it is suggested that the above isomerisation does not include a stage involving the intermediate formation of the cyclobutane derivative (XXXVII) (Scheme 10).[49]

Scheme 10



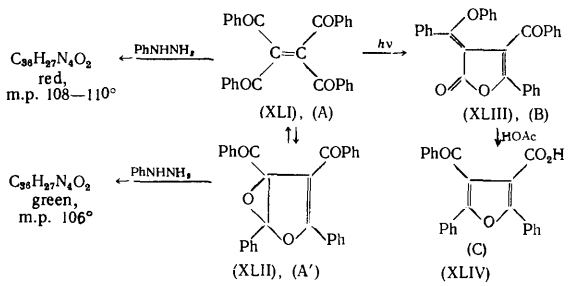
In order to investigate the factors influencing the solid-phase *cis–trans* transformations of compounds of the class considered, the structures of compound (XXXV), *trans*-1,2-ditolylethylene (XXXIX),[48] compound (XXXVI), and *cis*-1,2-bis(*p*-chlorobenzoyl)ethylene (XL)[50] were determined. Analysis of the molecular parameters indicates an appreciable loss of conjugation between the carbonyl and phenyl groups in compound (XXXV) compared with compound (XXXIX). The molecular packing in the crystals of compounds (XXXV) and (XXXIX) is of the stacked type and is not determined by the mutual contacts of the carbonyl group as in the *cis*-isomers (XXXVI) and (XL). The large distances between the centres of the double bonds [5.0 Å in compound (XXXV) and 5.4 Å in compound (XXXIX)] preclude the occurrence in this instance of solid-phase dimerisation reactions with formation of cyclobutane derivatives, which agrees with the data of Griffin et al.[49] The mutual orientation of the crystallographic axes of the phases (XXXV) and (XXXVI) has been determined from the X-ray diffraction pattern of compound (XXXV), on which reflections characteristic of compound (XXXVI) appear.[49] The packing density in the *cis*-isomer is somewhat smaller (the unit cell volumes are V_{cis} = 608.9 A^3 and V_{trans} = 596.1 A^3). The transition (XXXV) → (XXXVI) is accompanied by the loss of the centre of symmetry and leads to a change in the space group ($P2_1/c \rightarrow P2_1$). Even in the imperfect crystals of compound (XXXV)

the rate of rearrangement is low, i.e. the photoisomerisation apparently takes place in defective regions and is propagated via the dislocations formed around the nuclei of the *cis*-isomer.[48]

3. Isomerisation of Tetrabenzoylethylene

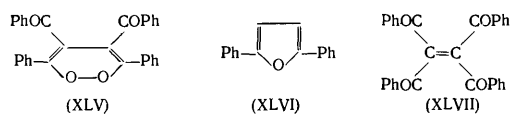
Tetrabenzoylethylene exists in three crystalline forms: two colourless forms (A) and (A') and in the yellow form (B), to which structures (XLI), (XLII), and (XLIII) respectively have been ascribed (Scheme 11).[51–55]

Scheme 11



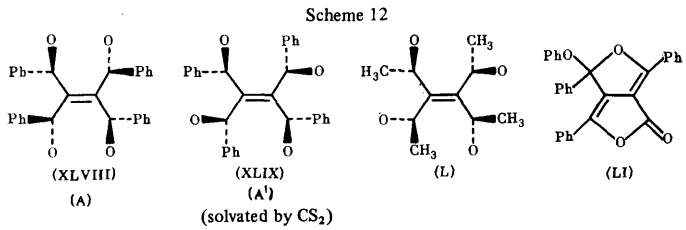
In daylight form (A), produced on crystallisation from a large amount of organic solvents, is irreversibly converted into form (B), whose treatment with acetic acid affords the product (C), to which the structure (XLIV) has been attributed. Crystals of compound (A') are obtained by crystallisation from CS_2 and are resistant to the action of light.

In addition, the structure (XLV) has been proposed[54] for compound (A'). The structure (XLIV) of the product (C) has been confirmed[55] by the formation of 2,5-diphenylfuran (XLVI) on its decomposition. Data for the tetra-acetyl derivative (XLVII) have been used in the analysis of the possible structure of tetrabenzoylethylene.[51–55]



It has been established by X-ray diffraction studies[56] that compounds (A) and (A') do indeed represent different crystalline modifications of tetrabenzoylethylene, the different types of behaviour of which on irradiation with visible light being explained by the difference between the conformations of their molecules and in their packing in the crystals. The conformations (XLVIII) and (XLIX) correspond to forms (A) and (A') respectively (Scheme 12). The related tetra-acetylethylene molecule has the conformation (L) in the crystal. In addition, X-ray diffraction study[57] has shown that the product (B) of the photolysis of (A) has the structure (LI) and not the structure (XLIII) proposed previously.[52]

Scheme 12

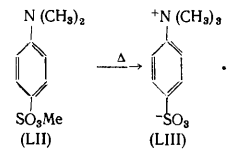


Intermolecular contact between the carbonyl oxygen atom and the hydrogen atoms in the *o*-positions in the ring has been observed in the crystal (A), its length being 2.62(8) Å, which is close to the sum of their van der Waals radii (2.72 Å).[35,36] A series of fairly short contacts involving the hydrogen atoms in the *m*-positions in the same ring have also been found. It may be that the intermolecular interaction in the direction of this O...H contact leads to the formation of a phenyl radical whose attack on a neighbouring molecule gives rise to the product (B); the generation of the next phenyl radical then leads to the propagation of reaction via chain mechanism along the *a* crystallographic axis.[42]

At the same time the authors[57] do not rule out the possibility of an intramolecular rearrangement of compound (XLVIII) to compound (LI). As a consequence of the alternation of the deviations of the parallel groups from the plane of the ethylene fragment in the molecule of compound (XLVIII), there is a possibility of forming hydrogen bonds between the carbonyl oxygen atoms and the *o*-hydrogen atoms of the neighbouring benzoyl groups. In addition, the alternating disposition of the benzoyl groups in compound (XLVIII) relative to the plane of the ethylene group prevents a concerted intramolecular movement of the phenyl groups. The disposition of the oxygen atoms in compound (XLVIII) favours the formation of the condensed furo[3,4-*c*]furan system (LI).

4. Rearrangement of Methyl *p*-Dimethylaminobenzenesulphonate

Methyl *p*-dimethylaminobenzenesulphonate (LII) rearranges in the solid phase to the betaine (LIII), the rate of reaction increasing with temperature until the attainment of the melting point, after which it falls sharply:[58]



An X-ray diffraction study showed[58] that the crystals of compound (LII) is made up of stacks of molecules, whose arrangement is convenient for the transfer of the CH_3 group along the molecular chain. The impossibility of an intramolecular rearrangement has been demonstrated experimentally using the corresponding deuterio-derivatives.

The CH_3 transfer process has been modelled by calculating the energy of the interaction of the molecule of compound (LII) with the CH_3 group approaching it,[59] using the extended Hückel method. The initial molecular geometry was taken from X-ray diffraction data. The extent to which the CH_3 and $(CH_3)_2N$ groups are pyramidal was varied as a function of the increasing distance from the N and O atoms; it was assumed that the CH_3 group is planar and is located between the N and O atoms at equal distances from the latter.

Fig.1 presents the dependence of the energy of the system described on the O–CH_3 and N–CH_3 distances and the extent to which the CH_3 group has been withdrawn (λ_1 and λ_2). The energy surface was of the kind usual for reactions of the type X + YZ = XY + Z, but the presence of a minimum in the lower left-hand region, where a saddle point is normally present, is striking. The dashed line indicates the path corresponding to the formation of an adduct with subsequent abstraction of the ether CH_3 group. The mechanism of the formation of a new bond with simultaneous dissociation of the old one would correspond to a diagonal path on the energy surface. The need to overcome a significant energy barrier

in this path suggests a two-stage process mechanism involving the formation of the corresponding intermediate compound. The total activation energy for the process along this reaction path is low and the relative thermodynamic advantage of the product molecule compared with the initial molecule is equivalent to ~12 kcal mol^{-1}.

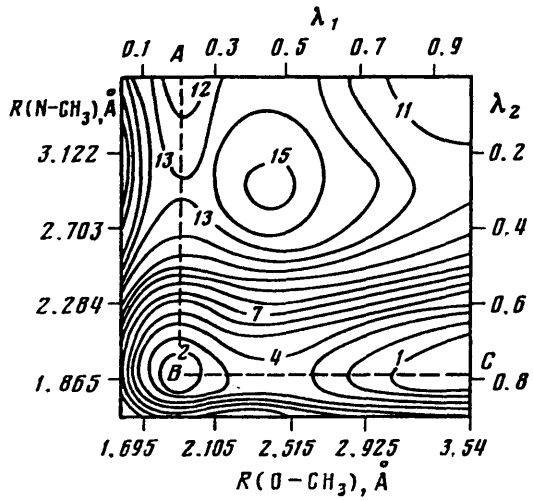


Figure 1. The energy surface for the reaction as a function of the distance to which the CH_3 groups are removed (λ_1 and λ_2) on dissociation of the O–CH_3 and N–CH_3 bonds. The energy contours are drawn at 1 kcal mol^{-1} intervals. Stage *A* corresponds to $^{+}CH_3 + (CH_3)_2NC_6H_4SO_3CH_3$, stage *B* corresponds to $(CH_3)_3\overset{+}{N}C_6H_4SO_3CH_3$, and stage *C* corresponds to $(CH_3)_3NC_6H_4SO_3^{-} + \dot{C}H_3$.[59]

The charges on the atoms and the Mulliken bond orders have been calculated for the molecules of the initial compound and the product. The CH_3 group abstracted has a large positive charge, which is partly transferred to the remaining CH_3 group. In the course of this rearrangement the negative charge on the N atoms becomes smaller and that on the O atom increases. The migrating CH_3 group leaves behind a bonding electron on the O atom, but at the same time it captures an electron from the N atom, which is used to form a new bond, so that the total change in the charge of the CH_3 groups should be small. The reaction involving the formation of methyl radicals does not then occur, since such a pathway would have involved a greater activation energy.

The change in the energy of the crystal structure as the CH_3 group moves towards a neighbouring molecule (and also as the character of the coordination of the N atoms is altered) in the course of the migration of the CH_3 group in the crystal was estimated by the method of atom–atom potentials,[68] taking into account the electrostatic component. The calculation showed that the displacement of the CH_3 group by 1 Å changes the energy of the crystal structure by only 7 kcal mol^{-1}. For the $(CH_3)_2N$ group, the deviation of the substituents towards the approaching CH_3 group is unfavourable, while that in the opposite direction is free (within the limits of 40°).

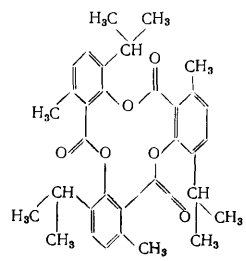
In order to elucidate the character of the changes in the molecular packing energy in the crystal on passing from compound (LII) to compound (LIII), the energy of the structure of compound (LII) was also calculated using the coordinates taken from the results of its X-ray diffraction study[58] together with the energy of a model crystal made up of molecules of compound (LIII) but packed in the (LII) lattice.[59] It was found that this hypothetical structure is significantly less favourable than the real structure of compound (LII). This is apparently in fact one of the reasons why the transformation described above does not proceed via a single crystal–single crystal mechanism.

Additional information about the mechanism of the reaction considered has been obtained from Raman phonon spectra,[60–62] which yield information both about the structure and the dynamics of the lattice, by means of which it is possible to obtain the characteristics of the homogeneity or heterogeneity of the solid-phase processes. The dynamics of the crystal lattice in which solid-phase reactions take place can favour their occurrence (the so-called "phonon enhancement"). In order to detect the possibility of such an enhancement, one considers the temperature dependence of the phonon spectra, where it is possible to observe a softening of certain modes, which indicates an increase in the amplitudes of the molecular movements precisely in the crystallographic directions along which solid-phase reactions can occur.

Analysis of the phonon spectra of crystals of compound (LII)[61] led to the conclusion that in this instance the solid-phase reaction is heterogeneous, which is consistent with the conclusions of Gavezzotti and Simonetta.[59] A study of the temperature dependence of the phonon spectrum revealed a softening of one of the modes (27 cm^{-1}), which indicates the possibility of the phonon enhancement of the reaction considered.

5. Geometrical Isomerisation of *cis*-Stilbene in Clathrate Complexes

The intramolecular solid-phase rearrangements in crystals made up of identical molecules were discussed above. Naturally, such reactions are possible also in clathrate compounds, where the reacting molecules are enclosed within cavities of the crystal lattice of the "host" molecules. Among the numerous known clathrate-forming compounds, the one which attracts most attention as regards the topic of the present review is tri-o-thymotide (TOT), which forms clathrates of different type,[63] a common feature of which is their chiral structure.[64] In particular, this gives rise to the possibility of the asymmetric synthesis in the reactions of prochiral "guest" molecules enclosed in the chiral TOT crystals.[65]



The first example of the photoinduced stereoisomerisation in crystals of TOT clathrates is the solid-phase rearrangement *cis*-stilbene.TOT–*trans*-stilbene.TOT under the influence of ultraviolet irradiation.[63] The reverse transition

in the crystal has not so far been observed, although in solution both processes are possible.[66] The quantitative *cis–trans* photoisomerisation has been thoroughly investigated also for crystalline olefins (for example, for cinnamic acid derivatives) in the absence of clathrate-forming compounds[7,67] and a common feature of all these processes is the absence of the reverse conversion of the *trans*-isomers into the *cis*-isomers. This constitutes the fundamental difference between the solid-phase processes of this kind and liquid-phase processes, although the rearrangements can take place in both directions.[63]

The conformations of the TOT molecules in crystals of the *cis*-stilbene.TOT (LIV) and *trans*-stilbene.TOT (LV) clathrates are very similar.[63] In the crystal of compound (LV) two symmetrically independent (i.e. not linked by the symmetry elements of the space group) stilbene molecules are located at the centre of symmetry, fill the non-intersecting channels parallel to the *a* and *b* crystallographic axes respectively, and are disordered (statistically or dynamically), which is manifested by high thermal parameters of their atoms. The characteristic features of the molecules incorporated in various inclusion complexes are in general either complete orientational disorder, which can be detected in certain cases by NMR in the solid state,[64] or a fairly high order, the extent of which, for example in the case of compound (XL), can be reliably determined by X-ray diffraction.

The packing of symmetrically independent *trans*-stilbene molecules in the above two types of channels of one (LV) crystal differs as regards the C...C distances between neighbouring molecules in the channel of each given type (4.60 and 3.83 Å) and the distances between the planes passing through the aromatic rings of neighbouring molecules (0.6 and 2.0 Å). The *cis*-stilbene molecules in the crystal of compound (LIV) are disordered with respect to two positions (linked by a centre of symmetry), the overall population of which is lower than that of the populations of the positions of the *trans*-stilbene in the crystal of compound (LV).

Table 2. The volume of the channels in the clathrates (LIV) and (LV).[63]

Channel	V_f, Å^3	V_u, Å^3
a-Channel (LV)	570	94
a-Channel (LIV)	570	72
b-Channel (LV)	826	56
b-Channel (LIV)	887	103

Notation: V_f is the free volume in the TOT matrix and V_u the useful volume (accessible to the "guest" molecules).

The reactions of the occluded molecules in clathrates require a preliminary alteration of the shape and volume of the channels; the very similar densities and unit cell parameters of the clathrates (LIV) and (LV) indicate an insignificant alteration of the free volume in the TOT matrix. Table 2 shows that, whereas the overall volume of all the cavities (the free volume) in the TOT matrix changes insignificantly in the (LIV) → (LV) transition, its component in which the "guest" molecules can be accommodated (the useful volume) undergoes an appreciable change (namely there is a sharp alteration in the *b* channels and a smaller alteration in the *a* channels), which can be accounted for by a change in the shape of the channels, while the volume remains unaltered.

The reason why *trans*-stilbene is preferentially incorporated in TOT may be associated with the mutual correspondence of the symmetries of the "guest" molecule and of the cavity in the matrix of the "host" molecule. The absence of a centre of symmetry in the *cis*-stilbene molecules creates less favourable conditions for their packing in a centrosymmetrical cavity, as a result of which the corresponding clathrate is less stable. It is useful to take this into account in seeking suitable molecules for inclusion in the lattice of the given "host". For example, one may expect that, for a "host" forming centrosymmetrical cavities, the *meso*-(*R*,*S*)-diastereoisomers are preferable to the D- or L-(*RR* or *SS*)-stereoisomers, while the inclusion of molecules of the second type will be preferable in cavities having the C_2 symmetry.

When any solid-phase chemical reaction is considered, provided that it differs from the corresponding reaction in solution, the question arises in what way and at what stages does the crystalline medium exert its influence on the course of the reaction. Thermal solid-phase reactions can therefore be usefully subdivided into four stages: the initial "loosening" of the molecular packing in the "reaction centre" of the crystal, their subsequent intra- or inter-molecular chemical transformation, then the formation of a solid solution of the product in the initial substrate, and finally the concluding separation of the product phase.[10] In photochemical solid-phase reactions the first stage as such is naturally absent, its role being assumed by the photoexcitation of the crystal system.

The photoisomerisation reactions in TOT clathrates can be regarded as processes occurring in the closed volume of the "reaction cavity" of the clathrate. An alternative explanation is that the molecules can diffuse from the closed cavities of the clathrate into its less "constrained" positions, in which they initially undergo chemical transformations and this is followed by the recrystallisation of TOT and the reaction product (*trans*-stilbene) with formation of the final clathrate. Although the second pathway cannot in fact be fully ruled out, preference has been given[63] to the process in the "reaction cavity".

As regards the solid-phase transition (LIV) → (LV), it has been concluded[63] that the transformation of a molecule with C_1 symmetry into one with a C_i point group within the cavity having the same C_i symmetry is the main factor which determines the observed photochemical reaction. Since the *cis–trans* isomerisation of stilbene requires the internal rotation of one fragment of the molecule relative to the other by 180° and therefore presupposes a definite deformation of the reaction cavity, it has been suggested that this kind of deformation takes place readily in TOT clathrates, which has been confirmed, in particular, by the wide variety of molecules which can be incorporated in such clathrates.[63,67] The manifestation in the crystal of compound (LV) of a temperature dependence of the rate of the *cis–trans* isomerisation of stilbene, is apparently associated with a kind of activation of the "loosening" of the molecular packing in the corresponding cavity,[10,63] which promotes a freer internal rotation, necessary for the *cis–trans* isomerisation indicated. The breakdown of the ordered disposition of the molecules in TOT clathrates following this kind of loosening of the packing is not always reversible and, when the molecules do not return to their initial positions or when the concerted nature of their migration in various parts of the crystal is disturbed, then a transition of the single crystal–single crystal type does not take place and individual crystallites of the new phase are formed.

6. Isomerisation of the Monoadduct of 11-Cyano-1,6-Methano[10]Annulene and 4-Methyl-1,2,4-Triazoline-3,5-Dione

In the study of the liquid-phase Diels–Alder reactions between bridge [10]annulenes and *N*-methyl- and *N*-phenyltriazoindolines,[69] isomers of the *exo*-type [compounds (LVI)] and the *endo*-type [compounds (LVII)] of the monoadducts of 11-cyano-1,6-methano[10]annulene with 4-methyl-1,2,4-triazoline-3,5-dione were isolated (Fig. 2).[70] It was found that the interaction of compounds (LVI) and (LVII) with a second mole of 4-methyl-1,2,4-triazoline-3,5-dione leads to only one isomer of the bisadduct (LVIII), namely one having the *endo,endo*-configuration. Thus the initial monoadduct of the *exo*-type undergoes the configurational transformation (LVI) → (LVII) into the isomer of the *endo*-type before or in the course of the reaction with the dienophile.[69,71]

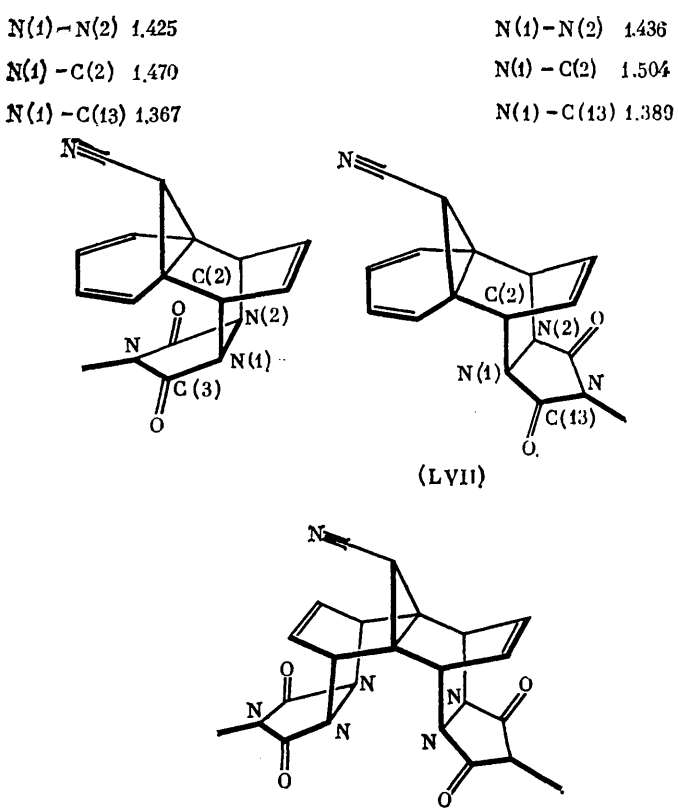


Figure 2. The structures of the *exo*- and *endo*-isomers (LVI) and (LVII) of the monoadduct and also of the *endo,endo*-isomer of the bisadduct (LVIII) of 11-cyano-1,6-methano-[10]annulene and 4-methyl-1,2,4-triazoline-3,5-dione.[71]

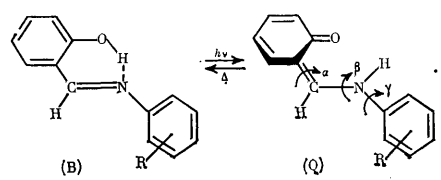
A similar study of the analogous solid-phase rearrangement (LVI) → (LVII) showed[71] that, on heating to 75 °C, dark bands appear within the (LVI) single crystal, although its outer form does not change. The complete transition (LVI) → (LVII) takes place at a temperature close to 175 °C: the X-ray diffraction patterns of compounds (LVI) and (LVII) become identical (when the powder method is used), and the reaction in the single crystal leads to the polycrystalline product (LVII). Of the two possible mechanisms of this process proposed for the solution, namely the Diels–Alder retro-reaction or or inversion relative to the N–N bridge in the primary adduct, the latter appears more probable. The barrier to the Diels–Alder retro-reaction of the model adduct of cyclopentadiene and maleic anhydride is 37.5 kcal mol^{-1}.[72] Since the C–N bond present in the molecule of compound (LVI) is only slightly weaker than the C–C bond in the model adduct, for compound (LVI) this barrier should be not less than 30 kcal mol^{-1}. In the case of double inversion the barrier should in its turn be only approximately 7 kcal mol^{-1} [for the (LVI) → (LVII) inversion] and ~9 kcal mol^{-1} [for the inversion (LVII) → (LVI)].[71] The experimental value is ~11.9 kcal mol^{-1},[71,73] which thus confirms the double N-inversion mechanism of the process under consideration.

Comparison of the geometrical parameters of the isomers (LVI) and (LVII) also confirms that the observed rearrangement proceeds via the mechanism involving the inversion of the N–N bridge. The less stable *exo*-isomer has a geometry closer to the flattened transition state of the isomerisation reaction considered. In fact, the dihedral angle between the planar fragments intersecting along the N–N bond in compound (LVI) (152.1°) is greater than in compound (LVII) (137.0°). The shortening of the bond between the hydrazine N atom and the C atom of the carbonyl group in the *exo*-isomer (LVI) thus also confirms the hypothesis that the planar transition state is stabilised by the conjugation of the diazo-group with the carbonyl group, which lowers the barrier to the inversion process.[71]

7. Chromotropic Reactions

Yet another large class of organic reactions which differ fundamentally when they are carried out in the liquid and crystalline phases comprises chromotropic transformations, in which the rearrangement is accompanied by a change in the colour of the reacting compounds. The arylimines of substituted salicylaldehydes are the most thoroughly investigated organic photochromic compounds in relation to this reaction (Scheme 13):[74,75]

Scheme 13



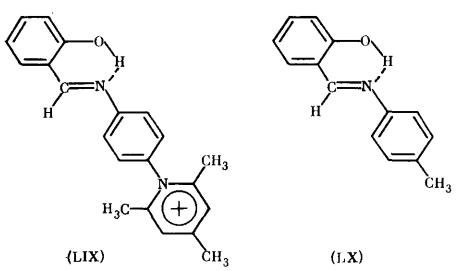
In solutions they are almost all photochromic, which is due to their ability to undergo on irradiation ($\lambda \cong 340–360$ nm) a rearrangement with phototransfer of a proton via the hydrogen bond from the O atom of the hydroxy-group to the imine N atom with transition of the planar benzenoid structure (B) into the quinonoid NH form (Q). As a consequence of the easier internal rotation of the fragments in the resulting (Q) molecule (with a change in the angles α and β and the rupture of the NH...O hydrogen bond), it now has a non-planar structure and is characterised by the appearance of the so-called "photochromic" absorption bands due to the different angles of rotation of the aldehyde ring in different molecules ($\lambda = 480$ nm, $\alpha \cong 50–55°$; $\lambda = 540$ nm, $\alpha \cong 65–70°$).[75–78]

The extremely short lifetimes of such (Q) structures in condensed phases ($\tau_{1/2} \cong 10^{-6}$ s) significantly hinder their study in solutions. However, in polymer matrices, frozen solutions, and in the crystalline phase, their lifetime is significantly increased, which explains the special advantages of the solid-phase methods for the investigation of chromotropic reactions compared with the liquid-phase methods.

Crystalline salicylidenearylamines (which are photochromic in solution) have been subdivided into two classes, which differ from one another as regards the character of physical influences inducing a change in their colour:[75] (1) photochromic non-fluorescent crystals which are coloured like the solutions, with the appearance in the absorption spectrum of bands at 485 and 540 nm, and which do not change colour when the temperature is altered; (2) thermochromic crystals which do not exhibit photochromic properties on irradiation but do fluoresce with a large Stokes shift at 77 K and are capable of acquiring a colour only on raising the temperature, whereupon a broad absorption band appears in their spectrum with a somewhat shorter wavelength in the range 400–470 nm.

Different types of behaviour of the compounds considered in solution and in the crystal justify the assumption that their photochromic and thermochromic properties in the crystalline state should be determined to a large extent by the influence of the packing.[75,79,80] This is confirmed by the formation of polymorphic photochromic and thermochromic modifications of salicylideneaniline[81] and salicylidene-*m*-chloroaniline[82] (depending on the rate of cooling of the solution on crystallisation) and also the photochromic and thermochromic solid solutions of compounds of this class, whose properties are determined exclusively by the crystal lattice of the "host".[83]

In order to elucidate the influence of intermolecular interactions and the nature of the phenomenon of chromotropism, the crystal structures of the photochromic (compound (LIX)] and thermochromic [compound (LX)] salicylidenearylamines have been compared.[75]



(LIX) (LX)

In the molecule of compound (LIX) $\alpha = 4°$, $\gamma = 51°$, and the angle of rotation of the trimethylpyridinium ring relative to the aniline ring is 87.2°. The molecules of compound (LX) in the crystal are planar and are packed in stacks along the c axis; the interplanar distance is ~3.4 Å. These data agree well with the results of other structural studies on compounds of this class[79,80,84–87] and show that the stacked close packing of the planar molecules is characteristic of thermochromic crystals and its absence and a non-planar molecular structure are characteristic of photochromic crystals.[75] Quantum-chemical calculation by the CNDO/2 method for the planar and non-planar ($\gamma = 60°$) molecules showed that the non-planar structure is preferable to the planar-structure only to the extent of ~2.5 kcal mol^{-1} [75] and the conformation of the molecules of compound (LIX) in the crystal can be fully determined by the packing effects.

The increased electron density at the N atom in the planar structure, which follows from the above calculation, strengthens the N...H–O hydrogen bonds, lowers the activation energy for the transfer of a proton from the O atom to the N atom in the ground state, and leads to the formation of the quinonoid form on raising the temperature. The formation of non-planar (in terms of the angles α and β) quinonoid forms of thermochromic compounds can be hindered by the stacked close packing of the planar molecules. Indeed calculation of the intermolecular interaction in the crystal of compound (LXX) by the method of atom–atom potentials yields 10.0 kcal mol^{-1} as the energy of the interaction between the molecules in the stacks, while the energy of interaction between the stacks does not exceed 2.5 kcal mol^{-1}.[75]

The non-planar photochromic molecules do not form close-packed stacks in the crystals, because the intermolecular interaction energy in such stacks does not exceed 1–3 kcal mol^{-1}. The non-planar molecular structure resulting from the decreased electron density at an N atom leads to an increased activation energy for the proton transfer in the ground state and the absence of thermochromism. However, on photoexcitation to the S_1 state, adiabatic proton transfer does occur.[75] In contrast to thermochromic crystals, in the photochromic structures the absence of a stacked structure in the latter entails the occurrence of an adiabatic non-coplanarisation process (with respect to the angles α and β), after the proton transfer, which no longer leads to fluorescence but to the formation of coloured forms with long-wavelength absorption at ~480 and 540 nm. The additional appearance in the spectra of thermochromic crystals of a long-wavelength absorption band at ~470 nm on raising the temperature can be associated with the formation of a certain amount of non-planar quinonoid forms, for example, on the surface of the crystal, as a result of an increase in the thermal vibrations of the atoms.

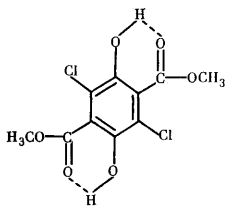
According to Aldoshin et al.,[75] the difference between the energies of the planar and non-planar forms of the free molecules of salicylidenearylamines is insignificant and is close to the intermolecular interaction energy in the crystal. If the gain in the crystal lattice energy is greater than the gain in the energy of the free molecule in one or other of the possible conformations, a structure arises in the crystal whose conformation ensures a minimum crystal lattice energy. Thus, by altering the ratio between the free energy of the molecule and the crystal lattice energy (by introducing various substituents), it is possible to regulate the structure and properties of the crystals.

A structural study[88] of the photochromic α_1- and α_2-forms of *N*-salicylidenepentafluoroaniline [compounds (LXI) and (LXII)], the α-form of *N*-salicylidene-4-bromoaniline (LXIII), and the thermochromic β-form of *N*-salicylidene-4-chloroaniline (LXIV) [the molecules of compounds (LXI)–(LXIII) are non-planar while those of compound (LXIV) are planar and packed in stacks] led to a mechanism of both types of chromotropic transitions based on the idea of the formation of intermolecular charge-transfer complexes (IRCTC). Thermochromic crystals are regarded in this case as an equilibrium mixture of tautomers, forming the corresponding IRCTC (the rate of equilibration depends on temperature). As regards photochromic crystals, their irradiation with ultraviolet light induces tautomerisation with formation of IRCTC [the crystals of compounds (LXI) and (LXII) have structures of the IRCTC type].

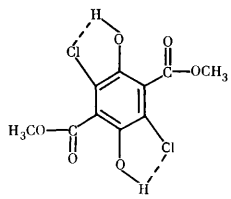
Investigations of solid-phase processes, which are close to phase transitions and in particular are close to the so-called conformational polymorphism in which a change in the conformation of the molecules in the crystal is accompanied by the

simultaneous alteration of structural and/or electronic characteristics of the system (intra- and inter-molecular hydrogen bonds, the colour of the crystal, etc.), can also be included among studies of intramolecular rearrangements.

The transition of the yellow form (LXV) of dimethyl 3,6-dichloro-2,5-dihydroxyterephthalate into the colourless form or, in the terminology of Curtin et al.,[89] the white form (LXVI), occurring on heating compound (LXV) to 140°, which is significantly below the melting point of compound (LXVI), is an example of this kind. The difference between the yellow and white forms, established by X-ray diffraction,[89] consists in the different dispositions of the intermolecular hydrogen bonds and also in the different orientations of the methoxycarbonyl groups relative to the plane of the benzene ring—in the yellow form these groups are in the plane of the benzene ring, while in the white form they are almost at right angles to it.



(LXV) yellow form



(LXVI) white form

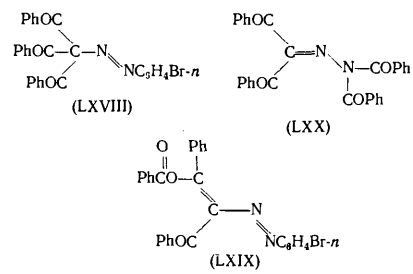
The difference between the characters of the intermolecular hydrogen bonds makes it possible to classify the molecules of the above two forms as isomers. Although the two forms crystallise in the same space group $P\bar{1}$, in the yellow form $Z = 1$ (one system of centres is occupied), while in the white form $Z = 2$ (two systems of centres are occupied), as a result of which the volume of the unit cell increases by a factor of two. The packing in the crystals of the yellow form consists of stacks of translationally linked molecules; the rearrangement of the packing occurring on transition to the white form can be described as the rotation of alternate molecules in the stack by 180° about the axis joining the Cl atom.

The rate of transformation of one form into the other depends significantly in this instance on temperature. Thus, whereas at room temperature both forms can coexist indefinitely, at 140° the transition takes place in several minutes. The transition can begin over a wide temperature range. Having been initiated at any point in the crystal, the new phase spreads in the [110] direction. When viewed through an optical microscope, this process appears to be a transition of the single crystal–single crystal type, but X-ray diffraction data show that the specimen obtained is polycrystalline, although it can consist of fine single crystals having similar orientations.

For a more complete investigation of the kind of processes occurring in the transition considered, the recently proposed technique of Ramon phonon spectroscopy in the solid state was used.[60–62] The Raman spectra confirmed the presence of different systems of hydrogen bonds in compounds (LXV) and (LXVI).[62] It was observed that only in the initial stages, when the content of the white form is low, does the process proceed as a homogeneous reaction, after which it acquires a heterogeneous character. The study of the temperature dependence of the phonon spectrum did not reveal a soft mode in the latter, which might have indicated the occurrence of lattice vibrations favouring the process via a topochemical mechanism. It was therefore concluded[62] that the thermal rearrangement is of a dislocation type although its mechanism at the molecular level still remains obscure.

Other examples of solid-phase conformational transformations are the transition of 2-(4-methoxyphenyl)-1,4-benzoquinone (LXVII) from the yellow to the red form (in which the rings undergo a mutual rotation by 110° and an overall reorientation of the molecule takes place with appearance of an intermolecular donor–acceptor interaction[90]) and the thermochromic polymorphic transitions of naphthazarine[91–93] and diaminoterephthalic acid esters.[94]

The structural rearrangement in the thermochromic transitions (observed both in solution and in the crystal) of the yellow azotriketone [compound (LXVIII)] to the red (compound (LXIX)] and colourless [compound (LXX)] products is more significant.[95] These processes consist in the competing migration of the acyl group from the C atom to the O atom [the (LXVIII) → (LXIX) transition] and from the C atom to the N atom [the (LXVIII) → (LXX) transition].



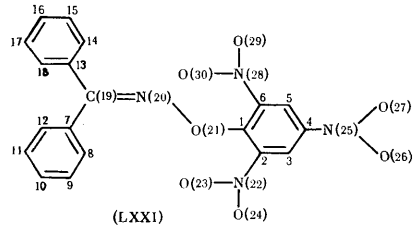
(LXVIII)

(LXX)

(LXIX)

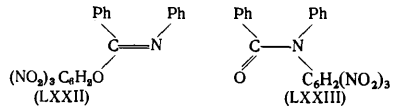
The ratio of the isomerisation products in the crystal and in the solution (dioxan) should then be fairly similar [(LXIX):(LXX) is 0.85 and 1.05 respectively]. The rate of reaction in the crystal is 100–400 times lower than in solution and diminishes as the quality of the crystals of compound (LXVIII) improves. If a more volatile solvent ($CHCl_3$) is used for crystallisation, then, when the resulting crystal of compound (LXVIII) is allowed to stand, the solvent diffuses from it and the rate of the thermochromic rearrangement increases (although the ratio of the red and white products is also altered).[96] Analysis of the non-valence contacts in the molecule of compound (LXVIII) did not reveal a structural preference for the migration of any particular acyl groups to the O or N atoms. At the same time the absence of intermolecular contacts from the crystal of compound (LXVIII) and the corresponding N, O, and C atoms in neighbouring molecules makes it impossible to attribute an intermolecular mechanism to the observed solid-phase thermochromism.[96]

An appreciable rearrangement of the molecule is observed also in the solid-phase thermochromic (≤70 °C) transformation of the colourless picryloxime (LXXI):



(LXXI)

and of its derivatives via the intermediate (LXXII) into the yellow amide (LXXIII):[96,97]

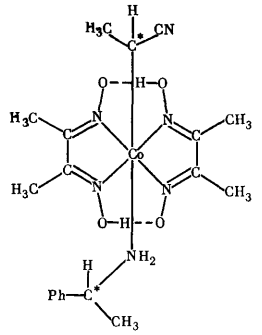


Steric strain is observed in the molecule of compound (LXXI) in the region of the O–Ph bond [C(1–6)], where the O(21), N(22), and N(28) atoms deviate from the plane of the benzene ring by −0.095, 0.144, and −0.134 Å respectively, while the N(25) atom in the *p*-position is located exactly in this plane. The C(6)C(1)O(21) and C(2)C(1)O(21) valence angles differ markedly (129.0° and 114.5°). The above geometrical distortions are caused by the intramolecular steric interaction of the N(20) atom and the nitro-group at the N(28) atom, on the one hand, and between the O(21) atom and the nitro-group at the N(22) atom, on the other [the N(20)...N(28), N(20)... O(30), O(21)...N(22), and O(21)...O(23) distances are 2.668, 2.859, 2.676, and 2.766 Å]. The aromatic C(7–12) ring in the *syn*-position relative to the picryl group has been rotated by a larger angle in the plane of the $C_2C{=}N(-O)$ group compared with the C(13–18) ring (60.5° and 18.6° respectively). The distance between the O(21) atom and the C(19) atom to which it migrates is 2.213 Å. Intermolecular distances less than 4 Å between the potentially reactive atoms in the crystal compound (LXXI) were not observed.[97]

8. Rearrangements of Metal Complexes

A structural study of *R*-α-cyanoethyl-(*S*-α-methylbenzylamino)cobaloxime (LXXIV) revealed a change in the unit cell parameters in the course of the X-ray diffraction which was not accompanied by the disruption of the single crystal.[98] After exposure for 22 days, a crystal of compound (LXXIV) [a = 8.665(2) Å, b = 13.485(3) Å, c = 9.584(3) Å, β = 96.95(3)°, V = 1111.6(5) Å^3; space group $P2_1$] is converted into a crystal of compound (LXXV) [a = 8.637(2) Å, b = 13.833(3) Å, c = 9.539(2) Å, β = 99.07(3)°, and V = 1125.5(4) Å^3]. A similar change in the unit cell parameters in the formation of a crystal of compound (LXXV) in the course of irradiation with X-rays has been established also for crystals of the second enantiomorphic form of compound (LXXIV).

Despite the retention of the non-centrosymmetric space group $P2_1$ of the initial compound for both types of crystals of compound (LXXV) formed, the two processes investigated represent the racemisation of the enantiomorphic forms of compound (LXXIV). An X-ray diffraction study[98] showed that, after the transition, the CH_3 groups of the cyanoethyl ligand occupy with equal probabilities two positions corresponding to the *R*- and *S*-configurations. It has been suggested[98] that this process proceeds via the dissociation of the Co–C bond and the appearance of the planar cyanoethyl radical capable of further recombination to reform the initial structures with equally probable attack on both sides in this reaction. This hypothesis has been confirmed by direct EPR observations of the homolytic cleavage of the Co–C bond in alkylaminocobaloximes when they are irradiated with visible light (λ > 420 nm).[99,100] The energy liberated on dissociation of the bonds can induce the formation of local zones consisting of the melt. The appearance of the racemic structure on re-formation of the bonds is apparently to be explained by its greater thermodynamic stability. The retention of the single crystal structure can be accounted for by the identity of the crystal-structure parameters of both enantiomers.



(LXXIV) and (LXXV)

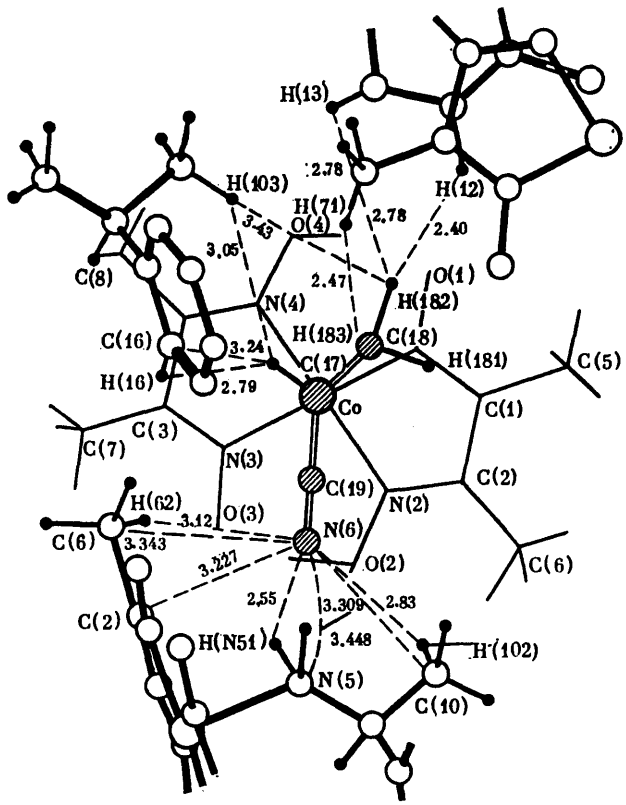


Figure 3. The environment of the atoms of the α-cyanoethyl group (shaded circles) in a crystal of compound (LXXIV); the C(17) atom is projected on to the Co atom.[98]

In order to investigate the dependence of the rate of the solid-phase racemisation of compound (LXXIV) on temperature, measurements have been made of the unit cell parameters of this compound at 133 K [a = 8.791(2) Å, b = 13.516(2) Å, c = 9.161(2) Å, and β = 98.31(3)°] and also their variation with increase of temperature to 293 K.[101] The difference between the parameters at 133 and 293 K is

unusual; on the one hand, it does not indicate the occurrence the (LXXIV) → (LXXV) transition, while, on the other hand, the explanation cannot be reduced to the thermal expansion of the crystals of compound (LXXIV) (the linear thermal expansion coefficients are -1.00×10^{-4}, -0.10×10^{4}, and 2.95×10^{-4} K^{-1} along the *a*, *b*, and *c* axes respectively). For the crystal of the racemate (LXXII) under the same conditions, the linear expansion coefficients are similar (-1.00×10^{-4}, 0.25×10^{-4}, and 2.50×10^{-4} K^{-1}), whence it follows that the thermal expansion of compound (LXXIV) [and possibly also of compound (LXXII)] is reversible.

Comparison of the crystal structures of compound (LXXIV) at 173 and 293 K has shown that cooling leads to the contraction of the crystal owing to the compaction of the structure in the region of the H(17) atom (Fig. 3). The most significant changes are in the H(17)...H(103) = 3.05 Å, H(17)...H(16) = 2.79 Å, and H(182)...H(103) = 3.43 Å, distances which diminish to 2.47, 2.53, and 2.56 Å respectively, i.e. the values corresponding to the normal van der Waals contacts. This compaction does in fact explain the retardation of the racemisation of compound (LXXI) at low temperatures.

Racemisation in the course of X-ray irradiation and its retardation on reducing the temperature to 133 K are also characteristic of crystals of the diastereoisomeric [in relation to compound (LXXIV)] complex *S*-α-cyanoethyl(*S*-α-methylbenzylamine)cobaloxime (LXXVI).[102] The crystals of compounds (LXXIV) and (LXXVI) have two features in common: (1) the molecules in the crystal have a bond which is sensitive to irradiation by X-rays and to exposure to electromagnetic radiation with a higher wavelength; (2) this bond is located in the region of loose packing (with increased intermolecular distances). However, in the case of the crystals of *R*-α-(methoxycarbonyl)ethyl(*R*-α-methylbenzylamine)bis(dimethylglyoximato(cobalt(III) racemisation is no longer observed, which is caused by the failure of the second of the conditions indicated in this instance.[103] Nevertheless, it is believed[101,103] that the number of crystalline complexes which satisfy both conditions should be large and that varied solid-phase reactions should be observed in them.

In contrast to compounds (LXXIV) and (LXXVI), the racemisation which takes place on irradiation of crystals of [(*S*)-1-cyanoethyl](pyridine)cobaloxime (LXXVII)[104] and [(*R*)-1-cyanoethyl](pyridine-4-carbonitrile)cobaloxime (LXXVIII),[105] which proceeds via the inversion of the configuration of the cyanoethyl group in one of the two [(A) and (B)] symmetrically independent molecules (in both cases the space group is P_1 with $Z = 2$), gives rise to the racemate (A'), whose molecules are characterised by an ordered disposition of the cyanoethyl groups (with a centrosymmetric space group $P\bar{1}$, Z = 1).

The volumes of the reaction cavities of the cyanoethyl groups in the enantiomorphic crystals of compounds (LXXVII) and (LXXVIII) and the crystals of the corresponding racemates are compared in Table 3 with the rate constants for racemisation in the crystal. The cyanoethyl group of the molecule (B), which undergoes inversion in racemisation, occupies a larger volume than the cyanoethyl group in the molecule (A). Evidently the greater the volume of such cavities, the higher the reaction rate. The retardation of the racemisation of the crystal of compound (LXXIV) at 173 K can also be attributed to a decrease of the volume of the cavity of the cyanoethyl group from 14.53 $Å^3$ at 273 K to 12.95 $Å^3$ at 173 K.[105] In the crystal of [(*R*)-1-cyanoethyl]-(4-methylpyridine)cobaltoxime, for which racemisation is also observed on irradiation, the cavities occupied by the reactive groups have a larger volume than those incorporating inactive groups.[105]

Yet another example of racemisation in the crystal has been described for the solid-phase transition on irradiation with X-rays of [(*R*)-1-methoxycarbonylethyl](pyridine)cobaloxime (LXXIX) containing the methoxycarbonylethyl groups $CH(CH_3)CO_2CH$ instead of the cyanoethyl groups.[106] The rate of racemisation of compound (LXXIX) (space group $P2_1$) is in this case so high that it has been possible to investigate by X-ray diffraction only the racemates of compound (LXXX) (space group $P2_1/n$).[105]

Table 3. The volume v of the cavities occupied by the cyanoethyl groups before (A and B) and after (A') the racemisation of compounds (LXXVII) and (LXXVIII) together with the rate constants *k* for the racemisation.[105]

Parameter	(LXXVII)	(LXXVIII)
v(A), Å³	7.97	8.89
v(B), Å³	10.37	11.34
v(A'), Å³	10.52	10.52
v(A+B), Å³	27.95	25.58
v(2A'), Å³	26.41	26.49
k, s^{-1}	$1.65 \cdot 10^{-6}$	$2.83 \cdot 10^{-6}$

9. Spin Isomerism

Many chemically and biologically important processes involving iron(II) and iron(III) complexes are accompanied by a change in the spin state of the metal atom. Such changes cause a sharp alteration in the strength of the donor ligand–metal ion bond and hence in the chemical properties of the complex; however, compounds manifesting the properties of "spin equilibrium", i.e. capable of existing in the form of an equilibrium mixture of spin isomers, have so far been little investigated.[107–112]

The crystallographic approach to the description of spin transitions both in the crystal and in solution involves the measurement at room temperature of the geometrical parameters of complexes with similar structures but with different spin states. For example, a study at room temperature of the low-spin complexes $[Fe(sal)_2trien]Cl.2H_2O$ and $[Fe(sal)_2.trien]NO_3.H_2O$ and the high-spin complexes $[Fe(acac)_2Cl_2.trien]PF_6$ and $[Fe(acac)_2trien]PF_6$(sal = salicylaldehyde, trien = triethylenetetramine, and acac = acetylacetone) revealed a difference of 0.12 Å between the average metal–ligand bond lengths.[113]

A more complete structural description of the spin isomers is provided by the X-ray diffraction study of the same object at high and low temperatures. Thus investigation of $Fe(2,2'\text{-bipy})_2.(NCS)_2$ (β-modification) at temperatures above and below the spin transition established a change in the Fe–N bond length from 2.02 Å in the state $^1A_1$ to 2.14 Å in the state $^5T_2$.[114] For the iron(II) complex with the hexadentate [4-(6-*R*)-2,2'-bipyridyl]-3-aza-3-butenylamine ligand,[115] the expected increase (by ~0.12 Å) of the average of the six Fe–N distances was observed on passing from the high-spin state at 300 K to a mixture of the high- and low-spin states at 205 K. The structure of iron(III) trisdithiocarbamate was determined at 79 K, where the complex exists predominantly in the low-spin state, and at room temperature, where there are approximately equal contents of iron in the high- and low-spin states.[116]

When the investigations are carried out at temperatures such that two or more isomers are present in large amounts, in all cases it is possible to observe only the "average" structure, i.e. the spin isomers are crystallographically indistinguishable. Crystallographic studies carried out at several temperatures, where the disorder caused by the presence of spin isomers can be experimentally differentiated, are therefore of greatest interest. We shall consider the X-ray diffraction study of the methanol solvate of tris(2-picolinylamine)iron(II) dichloride (LXXXI) carried out at five temperatures (115, 148, 171, 199, and 227 K).[117] The high- and low-spin isomers of this compound are well resolved at four temperatures in the range 148–227 K. The differences between the spin isomers are evident also from a comparison of the structural parameters of compound (LXXXI) at 148–171 K (where both spin isomers are present in appreciable amounts) with the parameters obtained at the highest and lowest of the selected temperatures of their measurements. The average distances between the low-spin iron atom and the nitrogen atom at 148 and 171 K are 2.01(1) and 2.02(2) Å respectively, whereas at 115 K, when the substance consists of 98% of the low-spin isomer, the difference is 2.016(3) Å. The average distances between the high-spin iron atom and the nitrogen atom at 148 and 171 K are in their turn 2.18(1) and 2.19(1) Å, while at 227 K, where compound (LXXXI) consists of 84% of the high-spin complex, the average distance is 2.198(6) Å.

Another criterion which makes it possible to distinguish the spin isomers is the presence of correlations between the thermal parameters of the corresponding ligand atoms in the low- and high-spin forms. The structure of compound (LXXXI) (at 148 and 171 K)[117] was refined on the assumption that the isotropic thermal parameters of all the atoms are independent. The physically reasonable values of these parameters even in those cases where the distances between the atoms of the low- and high-spin isomers are small is remarkable. In the crystal of compound (LXXXI) there exists a two-dimensional system of the Cl...H–N and Cl...H–O hydrogen bonds. Although it has been remarked that the nature of the hydrogen bonds in the spin-isomeric compounds can influence appreciably the spin equilibrium, a detailed analysis of the change in the system of hydrogen bonds in the crystal of compound (LXXXI) at different temperatures has not been carried out.[117]

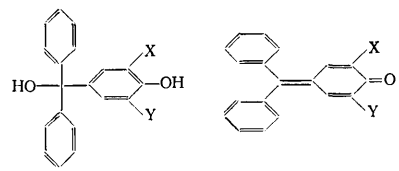
Estimates of the equilibrium constants for the spin transitions, obtained for compound (LXXXI) by X-ray diffraction[117] and by studying the Mössbauer effect,[118,119] have shown that the spin transitions in compound (LXXXI) are significantly non-cooperative; ΔH and ΔS are then 2.35(8) kcal mol^{-1} and 15.3(8) e.u. respectively, which may be compared, for example, with 4 kcal mol^{-1} and 10 e.u. for the spin transition in the complex tris [4-(6-*R*-2,2-bipyridyl)-3-azabutenylamine]iron(II) in the solid phase and in solution.[115] The above enthalpy change is apparently associated with the proximity of the spin transition temperature in these complexes to room temperature. In general the enthalpy change in the spin transition in the crystal is very sensitive to "specific" intermolecular interactions. On the other hand, one may expect that a change in entropy will not greatly influence the change in the crystal lattice observed during the course of the spin transition.[117]

III. REACTIONS WITH ELIMINATION OF SMALL MOLECULES

Chemical reactions in organic crystals accompanied by the liberation of low-molecular-weight products (in particular gaseous products) are well known. They include the desolvation of crystalline solvates (see, for example, Byrn and Lin[120] and Curtin and Paul[121]), controlled decomposition of explosive substances[122] and solid aza-compounds,[123] decarboxylation of diacyl peroxide,[124,125] and also the decarboxylation of *p*-aminosalicylic[126–129] and benzoic[130] acids.

1. Dehydration of *p*-Hydroxytriarylmethanols

The solid-phase thermal dehydration to the fuchsones (LXXXIII) of certain *p*-hydroxytriarylmethanols (LXXXII),[131,132] whose molecules have functional groups ensuring the presence in the crystal of a system of hydrogen bonds between the phenolic OH group (the proton donor) and the OH group at the sp^3 carbon atom (proton acceptor) in a neighbouring molecule, is well known. The presence of such hydrogen bonds, which link up the molecules into infinite chains, has been demonstrated by an X-ray diffraction study of compound (LXXXIIa) and also by the investigation of the isostructural crystals of compounds (LXXXIIb) and (LXXXIIc)[132,133]



(LXXXII): (a) X, Y=H; (b) X, Y=Br; (c) X, Y=CH_3; (d) X=CH_3, Y=H; (e) X=CH_3, Y=Br.

(LXXXIII): (a) X, Y=H; (b) X, Y=Br; (c) X, Y=CH_3

The thermal solid-phase dehydration of compound (LXXXII) in crystals having two different habits [(LXXXIIc′) and (LXXXIIc″) (Fig.4)] has been investigated.[133] The reactions in crystals of compound (LXXXIIc) proceeds in the same way as in crystals of compounds of a completely different type, namely certain oximes of picryl esters.[134–135] The reaction begins with the development at opposite end-faces of the crystal, namely (001) and (00$\bar{1}$), of readily distinguishable opaque triangular yellow regions, which consist of a solid solution of the reaction product in the initial crystal. The regions which have reacted crack and are then separated from the specimen. The [001] direction, in which the reaction is preferentially propagated, corresponds to the orientation of the hydrogen bond chains in the crystal of compound (LXXXIIc′).

The thermal dehydration of crystals of compound (LXXXIIc″) proceeds in a completely different way and begins immediately throughout the bulk of the crystal. It is striking that the crystal becomes yellow and turbid already at a low degree of conversion. Despite its identical structure, the thermal dehydration of compound (LXXXIIb) is approximately an order of magnitude faster than that of compound (LXXXIIc),[133] which can be attributed to the sharp (by a factor of 10^4) increase of acidity after the substitution of the CH_3 groups in 2,6-dimethylphenol by Br atoms.[136] However, the study of the rate of evolution of water vapour on heating the crystal showed that the monomethyl derivative (LXXXIId) is dehydrated much faster than the monobromo-derivative (LXXXIIe).[137] Unfortunately there are no structural data for compounds (LXXXIId) and (LXXXIIe).

The study of the photochemical dehydration of compound (LXXXII) (under ultraviolet irradiation) demonstrated that the reaction in both the single crystal and in polycrystalline

specimens (its visible manifestation consists in the appearance of a yellow colour and turbidity in the specimen) is observed only in thin surface layers.[133,136]

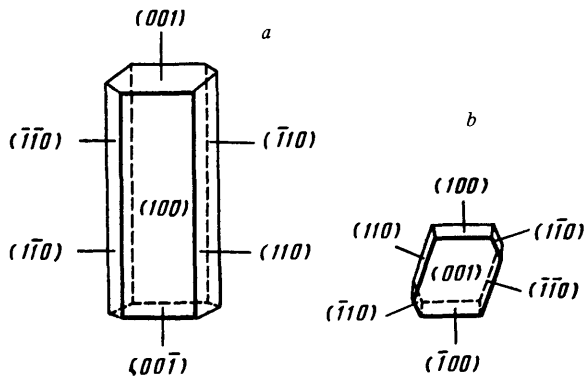


Figure 4. Two habits, (*a*) and (*b*), of crystals of compound (LXXXII).[133]

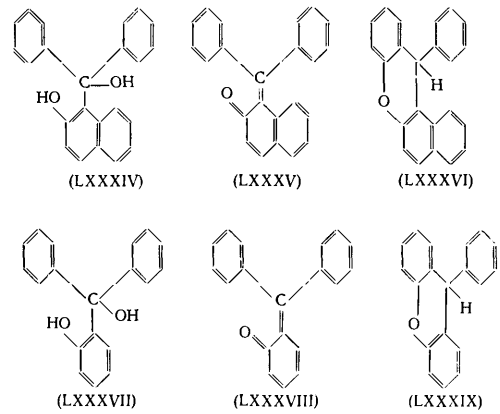
We may note that the crystal of (LXXXIIc) subjected to preliminary ultraviolet irradiation undergoes thermal dehydration much faster.[133] This is apparently caused by the photolytic formation in the crystal of the carbinol (LXXXII) of the nuclei of the fuchsone (LXXXIII) phase. It remains obscure how the fuchsone phase is propagated in the carbinol crystal: chemically, i.e. by transfer of the phenolic proton along the lattice defects, or in some other way.

As already stated, thermal solid-phase reactions in organic crystals have come to be described in terms of two limiting mechanisms, "heterogeneous" and "homogeneous", which have been used by Wegner et al. in the study of the solid-phase polymerisation of diacetylenes.[139] The heterogeneous reaction is characterised by an initial nucleation stage and subsequent migration of the reaction front through the crystal. The stage which determines the operation of one of the two reaction mechanisms is in fact nucleation. Both homogeneous and heterogeneous mechanisms are characteristic of the nucleation of the thermal dehydration of the carbinols (LXXXII), i.e. the process is the first example of a solid-phase reaction where the nucleation stage is under a kind of double control.[133]

The molecules of type (LXXXIII) can acquire chirality as a consequence of the internal rotation of their groups about single bonds. In the liquid phase the rapid interconversion of enantiomers should lead to the disappearance of chirality. However, in the solid phase, where the molecular conformation is frozen, there is a possibility of crystallisation in enantiomorphic space groups, as has been observed for binaphthyl (see, for example, Pincock and coworkers[140,141]).

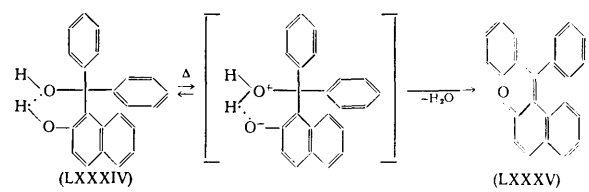
Three polymorphic modifications (α, β, and γ) have been observed for compound (LXXXIIIc), one of which, namely β-(LXXXIIIc), crystallises in the enantiomorphic space group $P2_12_12_1$.[142,143] X-Ray diffraction study revealed three types of deformations of the molecules of compound (LXXXIIc) in the crystals relative to the planar form: distortion of the quinone ring, breakdown of the planarity of the exocyclic double bond, and rotation of the aromatic rings relative to this bond. The crystals of α-(LXXXIIIc) and β-(LXXXIIIc) are made up of layers having similar structures but linked symmetrically to one another in different ways: via the 2_1 axes in β-(LXXXIIIc) and via the slip reflection planes and symmetry centres in α-(LXXXIIIc). The possibility of the thermal solid-phase transition α → β has been demonstrated[142] (by means of a powder diffraction pattern recorded at 383 K) and the changes in the geometry and packing of the molecules of compound (LXXXIIIc) required for this transition have been analysed.

In contrast to compound (LXXXVII), the solid-phase thermal dehydration of compounds (LXXXIV) and (LXXXVII) can proceed both intramolecularly [with formation of the fuchsones (LXXXV) and (LXXXVIII) and intermolecularly [with formation of the xanthenes (LXXXVI) and (LXXXIX).[144,145]



Later investigations[146] of the thermal dehydration of compounds (LXXXIV) and (LXXXVII) by infrared spectroscopy and NMR confirmed only the occurrence of the transitions (LXXXIV) → (LXXXV) and (LXXXVII) → (LXXXIX). X-Ray diffraction study[146] demonstrated the existence of intramolecular hydrogen bonds in crystals of compounds (LXXXIV) and (LXXXVII); thus the thermal dehydration in the crystals of compound (LXXXIV) probably proceeds via Scheme 14:

Scheme 14



An analogous mechanism of the intermolecular transfer of a hydrogen atom has been used to account for the thermochromic and photochromic transitions in crystals of salicylideneanilines (see, for example, Aldoshin and Atovmyan[147] and Cohen et al.[148]).

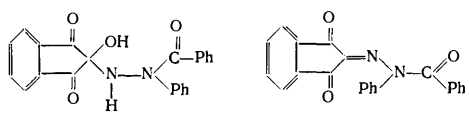
However, the discrepancy between the molecular geometries in the crystals of compounds (LXXXIV) and (LXXXVI) conflicts with the above description of the thermal dehydration of crystals of compound (LXXXIV). In fact the dihedral angle relative to the C(sp^3)–C(naphth.) bond in compound (LXXXIV) [as well as the corresponding angle in compound (LXXXVII)] is close to 80°, while an angle close to 0° (or 180°) would have been ideal for the rearrangement in accordance with Scheme 14. In a molecule of compound (LXXXV) the dihedral angles relative to the central double bond are 10.4° and 13.5° (two values are given in view of the breakdown of the planarity of the two central carbon atoms.[149] It has therefore been suggested[146] that the difference between

the solid-phase reactivities of compounds (LXXXIV) and (LXXXIIb) [the process (LXXXIIb) → (LXXXIIIb) is much faster than (LXXXIV) → (LXXXVI)] cannot be accounted for solely by the difference between the crystal structures of compounds (LXXXIV) and (LXXXVII).

The similarity of the crystal structures and hydrogen bond systems in compounds (LXXXIV) and (LXXXVII) makes it difficult to account for the difference between the products of their solid-phase thermal dehydration. It has been postulated[146] that the greater bulk of the naphthalene ring in the molecule of compound (LXXXIV) compared with that of the phenyl substituent in compound (LXXXVII) results in some flattening of the tetrahedron at the central sp^3-hybridised carbon atom, i.e. leads to a greater amount of sp^2-character in the latter. It may be that this difference between the geometries of the ground states of compounds (LXXXIV) and (LXXXVII) actually determines the difference between their reactivities in solid-phase dehydration processes.

2. Dehydration of (β-Benzoyl-β-Phenylhydrazyl)-2-Hydroxyindan-1,3-Dione

The solid-phase thermal dehydration of the hydrazinocarbinol (XC) proceeds anisotropically:[150] the appearance of the reaction product (XCI) [the acquisition of a red colour by the initial crystal of compound (XC)] begins at the $(10\bar{1})$ and $(\bar{1}01)$ faces and is propagated in the [001] direction.



After 17 days at 65 °C, the degree of conversion in the process (XC) → (XCI) is 10%. The possible sequence of stages in the solid-phase reactions of this type (nucleation, the formation of a solid solution, initiation of the new phase, and its separation) have been examined.[151]

The hydroxy-group O(4)–H in the molecule of compound (XC) in the crystal forms intramolecular hydrogen bonds with the carbonyl O(3) atom (Fig.5). The N(1)–H...O(2) hydrogen bonds between the molecules of compound (XC), linked by 2_1 axes, combine them into chains along the *b* axis of the crystal. Attack by a proton from the outer side of the chain (Fig.6) leads to the elimination of the OH group from the molecule of (A), which promotes also the subsequent abstraction of the OH group from a neighbouring molecule of (B) by the H(N) group. However, the H(N) atom forms a hydrogen bond with the O(1) carbonyl group of the molecule of (B) and not with the OH group; the H(N)...O(2) distance is 3.01 Å. The low rate of the reaction (XC) → (XCI) is apparently due precisely to the complexity of the rearrangement of the hydrogen bond formed by the N–H group. This hypothesis has been confirmed by the initiation of the reaction when a thin layer of the hydrate of toluene-*p*-sulphonic acid is deposited on the faces of the crystal of compound (XC),[151] the acceleration effect diminishing as the reaction front moves away from the region where the crystal is in contact with the acid. Fig.5 shows that the conformation of the molecule of compound (XC) is close to that necessary for the elimination of the H_2O molecule. During the reaction, there is an appreciable change in the geometry of the molecule of compound (XC), because its (H)OC(2)N(1)H(N) torsional angle is 36°, while in the indandione molecule the >C(2)=N(1) fragment should be planar.

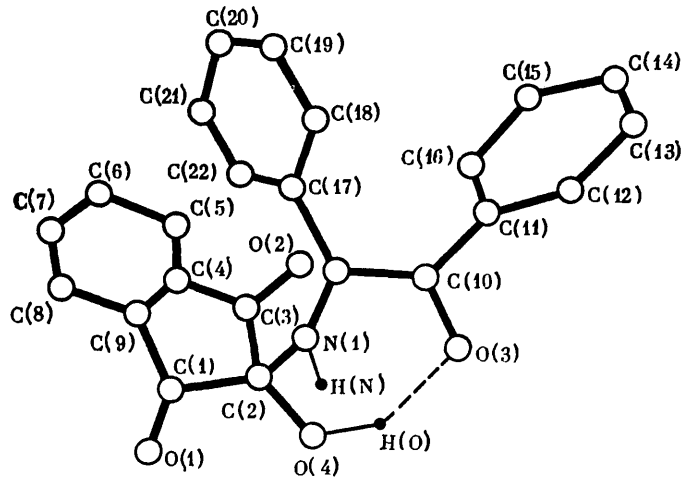


Figure 5. The structure of the molecule of compound (XC).[150]

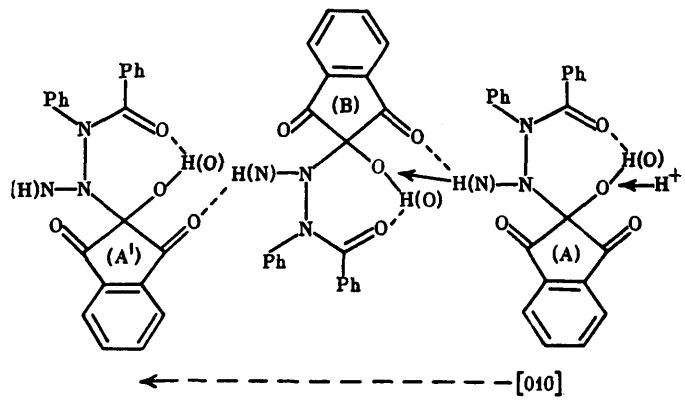
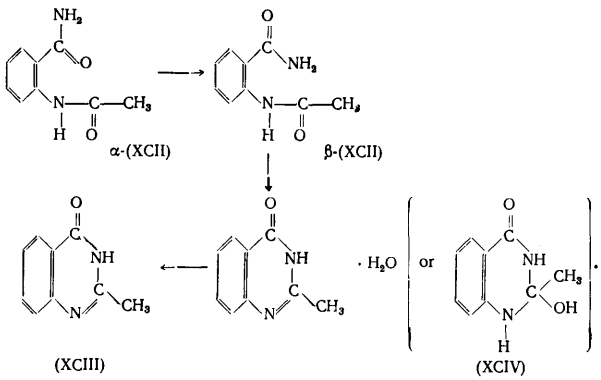


Figure 6. The possible mechanism of the solid-phase dehydration of compound (XC); the preferred direction [010] of dehydration is shown by a dashed line.[150]

3. Dehydration of *o*-Acetamidobenzamide

o-Acetamidobenzamide crystallises in two polymorphic modifications, α-(XCII) and β-(XCII), the solid-phase thermal transformation of which leads to anhydro-2-methyl-4-quinazolinone (XCIII).[152] Spectroscopic data and differential

scanning calorimetry indicate the following sequence of stages in the reaction (XCII) → (XCIII):



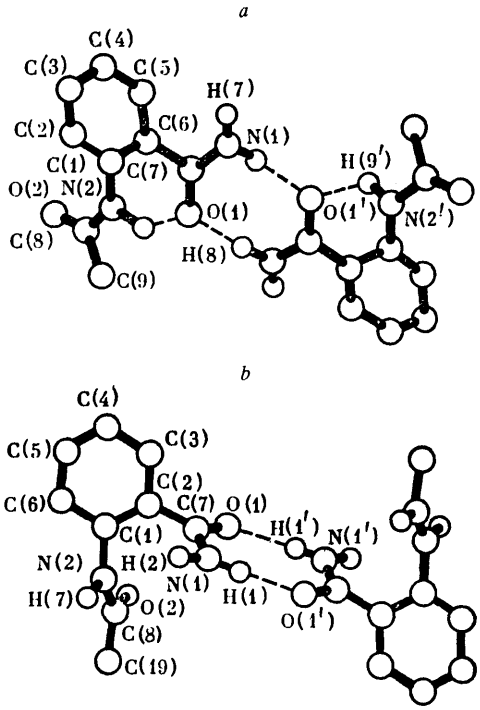


Figure 7. The structure of the centrosymmetric dimers in the crystals of α-(XCII) (*a*) and β-(XCII) (*b*).[152]

The crystals of α-(XCII) and β-(XCII) are made up of centrosymmetric molecular dimers (Fig.7) formed via a hydrogen bond with participation of the primary amido-group, the plane of the amide fragment in the structure β-(XCII) being inclined at 52° relative to the plane of the benzene ring, while in α-(XCII) the angle of inclination is only 8°. The appreciable difference of these angles from the energetically optimum value of 25° [152] has been explained by the simultaneous involvement of secondary *o*-amido-substituents in hydrogen bonds: the secondary amido-group in α-(XCII) participates in the intramolecular hydrogen bond with the primary amido-group, while in β-(XCII) it is involved in the intermolecular hydrogen bond between molecules linked only via the 2_1 axis. Fig.8 illustrates schematically the conformational transition α-(XCII) → β-(XCII) which is necessary for the formation of the system of hydrogen bonds observed in β-(XCII) crystals. Primary structural data for compound (XCIII) and the postulated structure of compound (XCIV) permit the conclusion that the main role in the destabilisation of the structure of β-(XCII), which leads to the solid-phase dehydration and the formation of compound (XCIII), is due to the hydrogen bonds combining the molecules of compound β-(XCII) into dimers.[151]

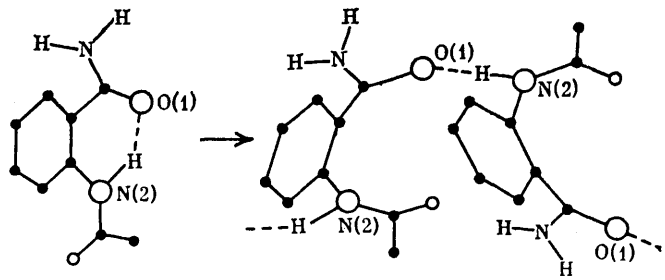


Figure 8. Schematic illustration of the conformational changes in the transition α-(XCII) → β-(XCII).[152]

X-Ray diffraction study of compound (XCIII) permitted hypotheses concerning the mechanism of its solid-phase hydrolysis with formation of compound (XCII).[153] The crystal structures of compounds (XCII) and (XCIII) are similar—the carbonyl groups in the molecules of compound (XCIII), linked via the 2_1 axis, form hydrophilic cavities parallel to the (001) plane. It has been suggested that the solid-phase hydrolysis of compound (XLIV) takes place precisely in the hydrophilic cavities along the *a* axis.

4. Dehydration of Copper Formate Hydrates

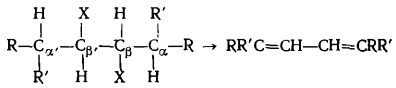
Crystals of copper(II) formate hydrates are known to be capable of thermal dehydration.[154–157] The structural treatment of this process, which is topotactic in character and leads to well oriented pseudomorphic anhydrous phases as products,[154,155,157] has been held back by the lack of structural data for such phases although the crystal structures of the initial copper(II) formate hydrates are known.[158–161]

The pale-blue crystals of copper(II) formate tetrahydrate $Cu(HCOO)_2.4H_2O$ (XCV) lose the water of crystallisation on drying in air and become opaque, being converted into the anhydrous phase $Cu(HCOO)_2$.[162] Comparison of the crystallographic parameters of compounds (XCV) and (XCVI) indicates the similarity of the structures in the *ab* planes and considerable differences between them in the direction of the *c* axis, which suggests the topotactic character of the dehydration of compound (XCV). A crystal of this compound is made up of layers, parallel to the (001) face, in which the copper atoms have a square planar environment consisting of four formate anions, each of which links two copper atoms. The H_2O molecules are distributed between these layers, half of them augmenting the coordination of the copper atoms to the octahedral coordination; the remaining water molecules are not coordinated at the metal atoms but form hydrogen

bonds with the H_2O molecules coordinated to the copper atoms.[162] The crystal of compound (XCVI) is also made up of layers of tetracoordinate copper atoms, analogous to those found in compound (XCV); the fifth and sixth coordination sites of the copper atom are occupied by the O atoms of the formate groups. Both types of molecules of water of crystallisation in the crystal of compound (XCV) have a relatively large amount of freedom as regards diffusion parallel to the layers. The removal of water should alter the coordination of the copper atoms and should lead to the mutual approach of the layers. Some structural rearrangement should occur also within the layers themselves.

5. Dehydrobromination of *meso*-dibromobutane Derivatives

Crystalline *meso*-dibromobutanes undergo double dehydrobromination on treatment with gaseous ammonia or amines, giving rise to quantitative yields of the corresponding buta-1,3-dienes[163]

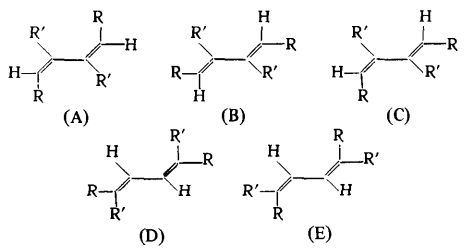


(XCVII)–(CI)

where (XCVII) = *meso*-β β′-dibromoadiponitrile, (XCVIII) = (*R*, *S*, *R*, *S*)-αα′-dimethyl-ββ′-dibromoadiponitrile, (XCIXa), (XCIXb) = (*R*, *R*, *S*, *S*)-αα′-dimethyl-ββ′-dibromoadiponitrile, (C) = dimethyl (*R*, *S*, *R*, *S*)-αα′-dimethyl-ββ′-dibromoadipate, and (CI) = dimethyl (*R*, *R*, *S*, *S*)-αα′-dimethyl-ββ′-dibromoadipate.

Apart from the van der Waals interactions, the molecular packing in crystals of compounds (XCVII)–(CI) is determined by the Br...N≡C and C...N≡C donor acceptor interactions.[164,165] The Br...N distances in the crystals of compounds (XCVII), (XCVIII), and (XCIXb) (3.20, 3.26, 3.22 Å respectively), which are significantly smaller than the sum of the van der Waals radii (3.45 Å),[35,36] can be regarded as corresponding to weak interactions between a Lewis acid and a Lewis base.[166] A weak interaction of the type C...N≡C is observed also in the crystal of compound (XCVII) (the corresponding C...N distance is 3.27 Å).

The solid-phase dehydrobromination of compound (XCVII) gives rise to a mixture of the isomeric butadienes (A)–(C) in the proportions 2:3:5, while the dehydrobromination of crystals of compounds (XCVIII), (XCIX), (C), and (CI) yields the pure products (B), (A), (D), and (E) respectively.[164,167]

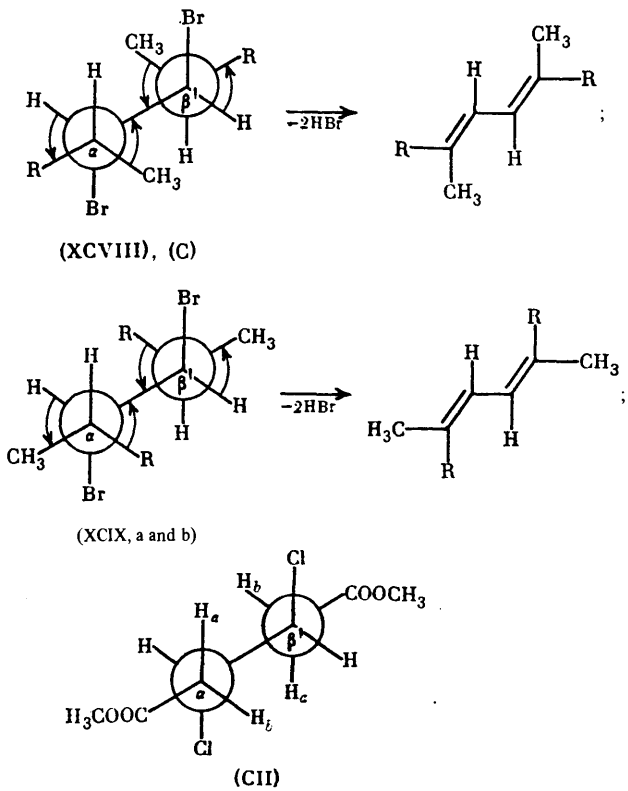


(A) (B) (C) (D) (E)

The reaction of the crystals of compound (XCIXa) is faster than in another polymorphic modification (XCIXb) of this compound.

In the crystals of the αα′-dimethyl derivatives of compounds (XCVIII), (XCIXa), (XCIXb), (C), and (CI), in which there is a possibility of the elimination of only one hydrogen atom from each C_α atom, all the H_α atoms are in the antiperiplanar positions relative to the Br atom. Assuming an *anti*-elimination mechanism, which requires a minimal rearrangement of the geometry of the carbon atoms for transition to the sp^2-hybridised state, one should expect the formation of the corresponding *trans,trans*-butadienes from the molecules of compounds (XCVIII) and (C) having the *R*, *S*, *R*, *S*-configuration and of *cis*-butadienes from the molecules of compounds (XCIX, a and b) and (CI) having the *R*, *R*, *S*, *S*-configuration (Scheme 15). This hypothesis has been confirmed experimentally[164,167] and it has demonstrated that the *anti*-elimination processes and the configuration of the products under the conditions of the heterogeneous gas–crystal reaction are controlled by the conformation of the initial molecules.

Scheme 15



(XCVIII), (C)

(XCIX, a and b)

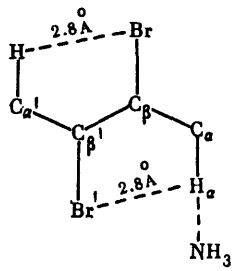
(CII)

The mechanism for the elimination reaction in molecules with two hydrogen atoms at each C_α atom is more complex. In the nitrile (XCVII) and the ester (CII) the H_a atom is antiperiplanar relative to the Br atom, while the H_b atom has a *gauche*-orientation. Since the *anti*-elimination mechanism applies also to the nitriles and esters, presumably the *cis,cis*-butadiene and the *trans,trans*-butadiene are formed respectively from compounds (XCVII) and (C). This course for the elimination process is consistent with the experimental data for compound (C),[164] but has not been confirmed for compound (XCVII). The formation in the latter case of a mixture of butadiene isomers shows that the elimination was preceded by rotation about the C_α–C_β bond in some of the molecules of compound (XCVII). Such rotation, which requires an energy expenditure of 5 kcal mol^{-1} according to conformational calculations,[168] is impossible in the crystal matrix, but, on the crystal surface and at the dislocations, where the reaction is initiated, the lattice is somewhat "staggered" and this barrier can be overcome.

We shall consider how, within the framework of the steric control of the *anti*-elimination in the crystal, the NH_4^+ ion is formed on one side of the molecule and a halide ion is

removed on the other (charge separation). It may be that, by virtue of the relatively short distance between the H_α and Br atom (~2.8 Å), the NH_4^+ ion, formed on the side of the C_α atom, induces the elimination of the Br′ atom linked to the C'_β atom, while the non-solvated Br^- anion, formed at the C_β atom, behaves as a strong base capable of abstracting the hydrogen atom linked to the C'_α atom (Scheme 16). The closeness of the oppositely charged ions leads to the subsequent rapid interaction.

Scheme 16



The induction period, frequently observed in reactions of the gas–crystal type,[169] as well as the influence of defects on the rate of these solid-phase processes[168,169] have shown that they begin with the diffusion of gas molecules to the existing nucleation centres (for example, to dislocations and impurities) at which the reaction is initiated and is then propagated throughout the bulk of the crystal.

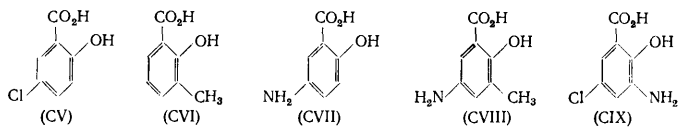
The difference between the types of packing should lead to a difference between the rates of diffusion and it is to be expected that the reaction should be faster in the less dense crystalline forms where the crystal field hindering diffusion is usually weaker. Apparently this is the explanation of the higher rate of dehydrobromination in crystals of compound (XCIXa) compared with (XCIXb), since the density of compound (XCIXa) is less than that of (XCIXb) (d = 1.84 and 1.90 g cm^{-3} respectively), while the intermolecular forces in the former case are weaker, which can be seen from the greater intensity of the thermal movement of atoms in the crystals of compound (XCIXa) at room temperature. The difference between the rates of diffusion of Br atoms, which is a consequence of the anisotropy of the crystal packing, has also been invoked to account for the different rates of bromination reactions of the gas–crystal type of the polymorphic forms of mesaconic acid.[169]

According to microscopic studies, reactions of the gas–crystal type are heterogeneous,[168,170,171] beginning on the surface of the crystal, while the process determining their rate is the "unpacking" of the layer formed, which hinders the movement of gas to the next layer. The observed difference between the rates of reaction in different crystallographic directions is usually interpreted on the basis of the idea that the reacting groups are unequally accessible to the diffusing gas molecules on different crystal faces. The anisotropy of the propagation of the reaction front is also observed in solid-phase rearrangements with thermal initiation.

We shall consider the possibilities of access to the potentially reactive hydrogen atoms on different faces of (XCIXa) and (XCIXb) crystals. The approach of NH_3 molecules to the H_α atoms can be blocked by the CH_3, CN, and C_β groups. The molecules in the crystal of compound (XCIXa) form layers perpendicular to the *b* axis and in each layer they are linked solely by *a* and *c* translations. The C_α–H bonds are perpendicular to the plane of the layer, while all the remaining bonds of the tetrahedral C_α atom are located approximately in the plane of the layer. In such a structure of the crystal, the neighbouring molecules located in a single layer do not hinder the approach of NH_3 molecules to the H_α atoms. The initial elimination of one H_α atom, which leads to the formation of NH_4^+ and Br^-, induces the elimination of a second H_α atom and results in a weakening of the fixation of the reacting molecule within the plane of the layer. The rate of the second process depends on the crystal forces, which are weaker in compound (XCIXa) than in (XCIXb). The partial "unpacking" of the layer ensures the access of NH_3 molecules to the next molecular layer. The H_α atoms of the molecular layer in compound (XCIXb) are much less accessible than in (XCIXa), which explains the lower rate of dehydrohalogenation of this crystalline modification.

6. Dehydrochlorination and Decarboxylation of *p*-Substituted Derivatives of Salicylic Acid

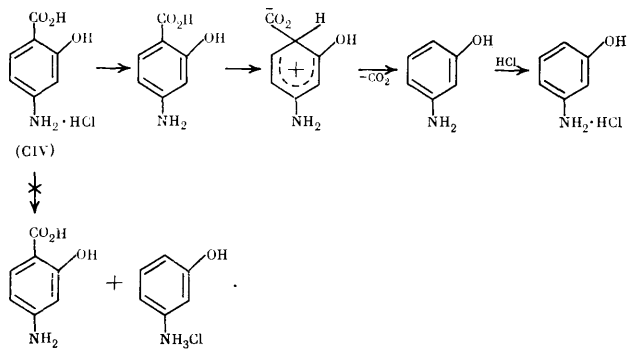
The kinetics and mechanism of the decarboxylation of *p*-substituted derivatives of salicylic acid in solution have been thoroughly investigated.[126–129] Solid *p*-aminosalicylic acid (CIII) decomposes at 70 °C, while its hydrochloride (CIV) decomposes at 100 °C. On heating to 100 °C, compound (CIV) is fully converted into *m*-aminophenol in 10 h. The salicylic acids (CV)–(CIX) did not decompose appreciably on heating to 100 °C for a week.



On the basis of kinetic data, a carbanionic mechanism of the decarboxylation reaction, similar to that observed for the decarboxylation of trinitrobenzoic acid, has been suggested.[172]

The decarboxylation of compound (CIV) involves the initial loss of HCl, which is followed by the decarboxylation, the sublimation of *m*-aminophenol, and finally its reverse interaction with HCl (Scheme 17). This sequence of stages agrees with the absence of a reaction of the crystal–crystal type between *m*-aminophenol and compound (CIV) when they come into direct contact.

Scheme 17



It has been stated[172] that this mechanism agrees with the characteristic features of the molecular packing in the crystals of compound (CIV). In conformity with the idea that solid-phase photochemical interaction between C=C bonds separated by a distance of ~4 Å is possible,[173] there exist four intermolecular contacts in the crystals of compound (CIV) between the acid proton and the unco-atom of the carbon ring attached to the carboxy-group, whose lengths are 3.98, 4.99, 4.60, and 4.42(3) Å, which gives rise to the possibility

of the propagation of the reaction in the crystal in several directions. The reaction is initiated on the $(10\bar{2})$ faces. Layers of polar carboxy-groups and non-polar aromatic groups, arranged parallel to the (100) face, are approximately perpendicular to the $(10\bar{2})$ faces. Thus the evolution of the CO_2 formed is to be expected from the side of the $(10\bar{2})$ face and not the (100) face.[169]

The solid-phase thermal (at 95 °C) decarboxylation of crystals of compound (CIV) having different habits (A, B, and C) has been investigated;[174] for this purpose, the development of the region of turbidity in the crystal (which corresponds to the disordering induced by the loss of HCl preceding the decarboxylation) was observed. In a crystal of compound (CIV) having the A habit, HCl is evolved along the *b* axis. The reaction along the *c* axis is slower. The loss of HCl by crystals of compound (CIV) having the B habit takes place in the direction of the *a* axis. If we now turn to the molecular packing in the crystal of compound (CIV), it is found that the HCl molecules can leave the crystal along the *a* and *b* directions without involving the non-polar functional groups and interacting only with the amino- and carboxy-groups. The evolution of HCl along the *c* direction is also possible, although in this case Cl^- ions and OH and NH_2 groups as well as hydrocarbon radicals may be encountered in the path of the HCl molecules.

Thus, the characteristics of the molecular packing suggest that the dehydrochlorination reaction should proceed along the *a* and *b* directions. The authors[174] were unable to explain the observed course of the reaction, which started from the $(0\bar{1}1)$, (011), and $(10\bar{2})$ faces of the form A of the (CIV) crystal. The attempts to explain the characteristic directions of propagation of the solid-phase reaction in a crystal of compound (CIV) having the B habit on the basis of the characteristic features of the molecular packing in the crystal were also unsuccessful.# Apparently the anisotropic loss of HCl by (CIII) and (CIV) crystals is associated with the characteristic features of the initiation of the reaction. The zone of the reaction initiated on a certain face of the crystal (having the A or B habit) migrates to its centre, and HCl is most easily removed via the regions which have reacted or been disrupted.[174]§

According to microscopic observations, the reaction in the *a* direction of the (CIV) crystal is faster than in the *b* direction, in conformity with the calculated cross-section of the tunnel for the release of HCl, which amounts to 3.23 $Å^2$ along the *a* axis and to 1.60 $Å^2$ along the *b* axis. The distance between the rings in the direction of the *a* axis is also smaller than in the direction of the *b* axis (5.316 and 4.232 Å respectively).[174]

The interaction of (CIV) crystals having the A and B habits with gaseous primary, secondary, and tertiary amines has been investigated.[174] The interaction with primary and secondary amines proceeds rapidly and leads to liquid products. However, hexamethylenetetramine reacts at the (001) face in the A crystal habit (in the course of 30 min), while crystals having the B habit [with (001) and (100) faces having a large area] do not decompose even after 72 h. Different rates of reaction with hexamethylenetetramine are also characteristic of the different faces of the acetylsalicylic acid crystal. There exist data demonstrating different rates of interaction of crystalline aminoacid enantiomers with optically active amines.[177]

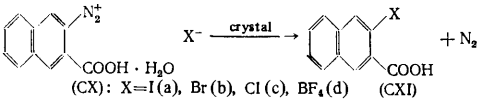
Crystals of compound (CIV) with all three habits are involved in an interaction of the crystal–crystal type with Na_2CO_3. This reaction always begins at the site of contact between the crystals of the acid and the carbonate and is fairly slow (it is completed after 40 days at 60 °C).[174] If the reaction occurs at room temperature, drops of water are formed. Compound (CIII) is formed as the product and *p*-aminosalicylate anions have also been detected. The low rate of reactions of the crystal–crystal type compared with those in solution can be accounted for by the low rates of diffusion of ions in the crystal lattice in compound (CIV).[178–182] If the solid-phase thermal decomposition of compound (CIV) in the absence of contact with Na_2CO_3 involves the loss of HCl by diffusion, then the reaction of the crystal–crystal type (acid–base) considered above consists either in the diffusion of HCl to Na_2CO_3 or in the counterdiffusion of H^+ or Na^+ ions with formation of H_2CO_3 in the lattice of the base and of NaCl in the lattice of the acid.

Reactions of the crystal–crystal type are relatively rare and have been thoroughly investigated only in relation to the formation of spinels from metal oxides (for example, Al_2O_3 and MgO) at high temperatures.[178–182] The most probable mechanism of these reactions is based precisely on the counterdiffusion of cations.

7. Decomposition of 3-Carboxynaphthalene-2-Diazonium Halides with Evolution of Nitrogen

Studies of the solid-phase reactions of aromatic diazonium salts began with the investigation of the thermal decomposition of solid benzenediazonium fluoroborate.[183] Aromatic diazonium salts readily explode and are isolated only rarely; nevertheless, a series of diazonium salts with weakly nucleophilic anions have been investigated by X-ray diffraction.[184–192]

We shall consider the mechanism of the decomposition of these salts in relation to the monohydrate (CX). The orange crystals of compound (CXa) rapidly acquire a blue colour on standing at room temperature, evolve nitrogen as a result of the substitution of its diazo-group by an I atom, and are converted into the polycrystalline acid (CXIa).[193–195] The intensity of the 2250 cm^{-1} band of the RN_2^+ group in the infrared spectrum diminishes rapidly. The topotaxy of crystals of compounds (CXa) and (CXIa) has not been observed.



(CX): X=I(a), Br(b), Cl(c), BF_4(d) (CXI)

The crystals of compounds (CXb) and (CXc) are isostructural and, like compound (CXd), crystallise as monohydrates. Data obtained by differential scanning calorimetry, thermogravimetric analysis, and X-ray diffraction indicate the ability of the triclinic crystals of compound (CXb) to lose water topotactically on heating about 65 °C and to be converted into an intermediate α-phase which is in itself then converted into the β-phase at 90 °C. The thermal decomposition of the β-phase (at ~100 °C) is accompanied by the evolution of nitrogen and the formation of 3-bromo-3-naphthoic acid (CXIb).[193–195]

#An analogous description of the propagation of a solid-phase reaction has also been resorted to to explain the loss of the water of solvation from the crystalline hydrates when the latter are cut by a razor blade[175] and in the solid-phase reaction of dimethyl 3,6-dichloro-2,5-dihydroxyterephthalate,[176] which begins at one end of the crystal and passes through the entire crystal in a direction which cannot be accounted for by the character of the molecular packing.

§Crystals of compound (XXIII) having the C habit have not been investigated by X-ray diffraction.

Although the molecular packing of the molecules in crystals of compounds (CXIa) and (CXIb) is of different types, the direct environment of the diazonium group in these compounds is similar: all the 15 C, N, and O atoms in the cations are approximately coplanar and there exists one shorter intramolecular O(13)...N(14) contact, whose length is 2.5 Å. The shortest intermolecular contact (2.9 Å) has been observed between the "outer" N(15) atom and the O(13) atom of the carbonyl group. The shortest contacts involving the halogen atom, namely I...N(15), which is 3.4 Å long in compound (CXIa), and Br...N(15), which is 3.27 Å long in compound (CXIb), also involve the outer N atom and are significantly shorter than the sum of the van der Waals radii (3.53 and 3.40 Å respectively[35,36]). The distances between the halogen atom and the "inner" N atom are 3.80 Å for compound (CXIa) and 3.50 Å for compound (CXb).

Each halogen atom is coordinated via two diazonium groups and is also involved in hydrogen bonds with the two solvating H_2O molecules [the Hal...OH_2 distances are 3.4 and 3.6 Å in compound (CXa) and 3.27 and 3.29 Å in compound (CXb)]. In addition, the H_2O molecule [O(16)] forms hydrogen bonds with carboxy-groups over O(12)...O(16) distances of 2.6 Å in compound (CXa) and 2.54 Å in compound (CXb) and is located opposite the C(2)–N(1) bond at a distance of 3.3 Å in compound (CXa) and 3.39 Å in compound (CXb) from the C(2) atom [the shortest intermolecular contact involving the C(2) atom].

The difference between the immediate environments of the diazonium groups in compounds (CXa) and (CXb) is determined by the van der Waals radii of the halogen atoms whose non-identity is manifested by the small differences between the corresponding Hal...N distances and also by the different intermolecular coordinations of the carbonyl O(13) atom.[193–195]

One may assume that the reactivity of compounds (CXa) and (CXb) is determined by the initial disposition of the halide and diazonium ions; N_2 is then evolved by a mechanism involving substitution as a result of attack by the halide ion. However, the discrepancy between the similarity of the environments of the diazonium group and the different stabilities of compounds (CXa) and (CXb) conflicts with this mechanism. The stability of the diazonium group in the β-phase (CXb) (~2 h at 95 °C) also conflicts with the alternative unimolecular mechanism involving the reversible loss of molecular nitrogen and the formation of aryl cations and relatively rapid cooling of compound (CXa) at 30–60 °C. The difference between the stabilities of the diazonium group combined with the similar environments in compounds (CXa) and (CXb) probably reflects the greater ease of oxidation of I^- ions compared with Br^- ions when an electron is transferred to the diazonium cation.[193–195]

The difference indicated between compounds (CXa) and (CXb) is intensified by virtue of the different character of the hydrogen bonds in the two structures, which link each halide ion to two molecules of water of crystallisation and also each water molecule to two halide ions. In the crystals of compounds (CXb) two bromide ions and two H_2O molecules are linked into rings around the centres of symmetry, while in compound (CXa) the hydrogen bonds form chains along the *c* axis made up of alternating iodide ions and H_2O molecules. The disruptions in the structure due to the absence of an H_2O molecule or the removal of a halide ion transmitted along the chain of hydrogen bonds [although it had not been possible to isolate the preferred direction of the disruption of the crystal of compound (CXa)]. When compound (CXb) is subjected to analogous disruption, there is a greater probability of the localisation of point defects, i.e. they do not spread throughout the bulk of the crystal.

The O–H...O hydrogen bonds and the short N(15)...O(13) intermolecular contacts in the crystals of compound (CXb) combine the cations into layers parallel to the $(1\bar{1}1)$ face; the shortest Br...N contacts are between the layers. The cracks appearing in the crystal of compound (CXb) in the transition (CXb) → α-(CXb) are perpendicular to the (001) face of the initial crystal of compound (CXb). It has been possible to establish a topotactic relation only with the fairly well ordered β-(CXb) phase, the volume of the unit cell of which proved to be smaller than for its hydrated precursor (CXb) (570 and 593 A^3). The $(\bar{1}1\bar{1})$ plane of the β-(CXb) crystal is inclined only at an angle of 14° to the $(1\bar{1}1)$ plane of the layers in the crystal of compound (CXb) and they both determine the direction of the cracks on dehydration of compound (CXb). It has therefore been suggested[190] that the layer structure of the crystals of compound (CXb) is preserved in the dehydration process and that the change (the disruption of the hydrogen bond system) takes place between the layers.

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Thus the intramolecular rearrangements and reactions with evolution of a low-molecular-weight product are characteristic of crystals of organic and complex compounds of a fairly wide variety of types. The degree of control of the course of these solid-phase reactions by the crystal lattices of the initial compounds in different reaction stages can be various.

The high selectivity of the majority of the reactions considered and the possibility of regulating them, at least in some cases, by altering the character of the molecular packing of the crystals of the initial compounds (crystal engineering) leads to extensive prospects for specific synthesis under the control of the lattice.

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Stabilisation of Disperse Systems by Water-soluble Polymers

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The stabilisation of disperse systems by the addition of uncharged and partly charged water-soluble polymers is considered. The influence of the adsorbed non-ionic polymers on various components of the interaction energy of the colloidal particles as well as the results of direct measurements of the repulsion forces between the adsorbed macromolecules are analysed. The mechanism of the stabilisation of real dispersions by adsorbed layers of uncharged macromolecular substances is discussed. The bibliography includes 141 references.

CONTENTS

I. Introduction 645
II. Rules governing the stabilisation of disperse systems by water-soluble polymers 645
III. Theoretical ideas concerning the stabilisation of colloidal solutions by adsorbed layers of non-ionic polymers 651
IV. The mechanism of the stabilisation of real dispersions by non-ionic polymers 655

I. INTRODUCTION

High-molecular weight compounds (HMC) are effective stabilisers of disperse systems and extremely small amounts of these substances can radically increase the stability of colloidal solutions as regards sedimentation and aggregation. This is used widely in various branches of modern technology: for the stabilisation of emulsions in the food, pharmaceutical, and cosmetic industries, in the manufacture of varnishes, dyes, paper, and photographic emulsions, in medicine, etc.

As early as the beginning of the 20th century, a study was made of the stabilising (protective) effect of the addition of hydrophilic substances (gelatine, starch, albumen, haemoglobin, etc.) on the hydrophobic sols of gold, silver, sulphur, and other colloids. Such substances are characterised by "gold", "silver", and other numbers.[1] Since the 1950s, synthetic polymers have been used on an increasingly wide scale for the stabilisation of dispersions, which led to an appreciable increase of the number of publications in this field during the last 15–20 years. Although many aspects of the influence of added HMC on the stability of colloidal solutions have been thoroughly investigated, the mechanism of the stabilising effect of polymers has not been finally elucidated and the theoretical principles of their selection for such purposes are in the initial stage of development. This is caused by the great complexity of the polymer-containing disperse systems and the multiplicity of factors responsible for their stability.

The stabilising effect of polymers in colloidal systems is directly related to their adsorption on the surface of the disperse phase. As a result of the adsorption of macromolecules or their aggregates,[2] the properties (including rheological properties[3]) of the interface and the intensity of the interaction between the surface and the intermicellar liquid are radically altered. This leads to a modification of the previous factors or to the appearance of new factors governing the stabilisation of the disperse systems; both effects are usually manifested. For a correct understanding of the mechanism of the action of HMC on the stability of colloidal solutions, it is necessary to have data on the adsorption of polymers by the disperse phase and the parameters of the adsorbed layers formed on the surface and on the influence of the adsorption of high-molecular-weight substances on the structure of the electrical double layer and on the hydration condition of the particles. Examination of the rules governing the adsorption of HMC by disperse particles and the structure of the electrical double layer is outside the framework of the present review; a discussion of these questions can be found, for example, in Refs. 4 and 5. Detailed information about the influence of the adsorption of HMC on the double layer and about the electro-surface methods for the determination of the parameters of the polymeric adsorption layers has been published.[6]

This review surveys the results of experimental and theoretical studies devoted to the elucidation of the rules and mechanism of the stabilisation of disperse systems by the addition of uncharged and partly charged water-soluble polymers, which have been published mainly during the last ten years. In particular, the methods for the measurement and for the theoretical calculation of the forces which determine the interaction of the polymer-containing particles have been examined.

II. RULES GOVERNING THE STABILISATION OF DISPERSE SYSTEMS BY WATER-SOLUBLE POLYMERS

As already mentioned, the influence of HMC on the stability of colloidal solutions is due to the characteristic features of the adsorption on the particles of the disperse phase and of the structure of the adsorbed layers formed under these conditions. However, the relation between the adsorption of the polymer and its influence on the stability was not considered in the vast majority of investigations, particularly in the earlier ones. The dependence of the stabilising effect of HMC on the nature and amount of the added reactant, its

molecular weight, the conditions in its introduction, the presence of electrolytes in the system, and other factors has been mainly investigated. We shall analyse briefly the influence of the above factors on the stabilisation of dispersions by high-molecular-weight substances.

1. The Nature of the Stabiliser

High-molecular-weight compounds, which, on the one hand, are adsorbed by the particles, and, on the other, readily dissolve in the dispersion medium, serve as stabilisers of dispersions. These are frequently copolymers, one of the components (A) of which is bound to the surface via chemical interactions, hydrogen bonds, etc., while the second component (B) exhibits a high affinity for the intermicellar liquid. For example, two polymers in which the role of component A is assumed by the substance which forms the disperse phase exhibit an effective stabilising activity towards latex dispersions. The inclusion in the composition of A of ionogenic groups bearing a charge opposite to that of the particles or highly polar functional groups significantly improves the bond between component A and the surface.[7] A polymer readily soluble in the dispersion medium and exhibiting a weak affinity for the surface is selected as component B. For aqueous media, such polymers are, for example, poly(ethylene oxide), poly(vinyl alcohol), poly(acrylic acid), etc., while for aliphatic hydrocarbons polyisobutylene, poly(lauryl methacrylate), etc. are used.[8]

In the systems considered component B forms a steric energy barrier necessary for stabilisation, while substance A ensures a bond with the surface. The ratio of the molecular weights of components A and B (M_A and M_B) is important for copolymers. As an approximation, one can assume that $M_A \cong nM_B$, where n is the number of polymer chains of B linked to the skeleton of A.[9] As a rule, M_A is in the range 10^4–10^5 and M_B is in the range 10^3–10^4.[8] The higher the adsorption energy of an elementary unit, the lower the value of M_A necessary to attain a satisfactory stabilising effect. M_B must be sufficiently large to ensure steric hindrance over distances ranging from several to several tens of nanometers from the surface; it depends on the size and chemical nature of the particles.

Substances with comparatively low molecular weights were used initially as stabilisers, namely carboxylic acids, alkylbenzenes, etc.—they were employed to obtain stable suspensions of carbon black, titanium oxides, iron, and other substances in organic solvents which are of practical importance.[8] High-molecular-weight compounds such as, for example, poly(vinyl alcohol) (PVA), poly(ethylene oxide) (PEO), methylcellulose (MC), non-hydrolysed and hydrolysed polyacrylamide (PAA and PAA-H), poly(acrylic acid) (PAAC), poly(methacrylic acid) (PMAAC) and its salts, polyethyleneimine (PEI), salts of carboxymethylcellulose (CMC) and polyvinylpyrrolidinone (PVP) and copolymers based on them, gelatine, and many others have been used recently to stabilise hydrodispersions. Table 1 lists examples of the employment of water-soluble polymers for the stabilisation of many model practically important dispersions.

As yet, it is difficult to formulate unambiguous criteria which would make it possible to decide which particular HMC would be the most effective stabilisers of a particular colloidal system. On the basis of theoretical considerations (see Section III) and the available experimental data, one can assume that, among non-ionic polymers, high-molecular-weight specimens which form fairly thick or fairly dense adsorbed layers on the surface of the particles will exhibit an effective stabilising activity. In the case of charged HMC, polyelectrolytes bearing like charges and having a high charge density on the macrochain would be more effective. The influence of the nature of the polymer on the stabilisation is to a large extent determined by the structure of the adsorbed layers formed on the surface, which depends on interactions of different types in the complex polymer-containing systems polymer–surface, polymer–solvent, polymer–polymer, and surface–solvent.[5,9] The stabilising effect of HMC depends not only on the degree of their polymerisation and the type and number of functional groups in the macromolecule but also on the character of the distribution of the latter along the polymer chain. Copolymers are as a rule more effective regulators of stability than homopolymers.[8]

Table 1. Water-soluble polymers used to stabilise disperse systems.

Polymer	Dispersion	
	of negatively charged particles	of positively charged particles
Non-ionic polymers		
Poly(ethylene oxide)	Au [10—13], AgI [14, 15], Sb_2S_3 [16]	AgI [14], Fe_2O_3 [12]
Poly(vinyl alcohol)	AgI [17, 18], AgBr [19], Sb_2S_3 [20], o/w [21, 22]	—
Poly(vinyl acetate)	AgBr [19]	—
Gelatine	AgI [23, 24], AgBr [19, 25], Au [1], SiO_2 [26]	AgBr [25, 27]
Methylcellulose	AgI [28], AgBr [25], Sb_2S_3 [28], latex [29], carbon black [30]	AgBr [25]
Unhydrolysed polyacrylamide	$Ca_3(PO_4)_2$ [31], SiO_2 [32]; kaolinite [32], MnO_2 [33]	CaF_2 [34]
Anionic polyelectrolytes		
Hydrolysed polyacrylamide	AgBr [35], MnO_2 [33], SiO_2 [36], latexes [37]	—
Sodium polystyrenesulphonate	Au [12], AgBr [35], latexes [39], montmorillonite [38]	Fe_2O_3 [12]
Poly(acrylic acid) and its salts	AgI [40], AgBr [35], SiO_2 [41], ZnS [43, 44], kaolin [45]	AgI [40], Al_2O_3 [41]
Sodium salt of carboxymethylcellulose	AgI [46], Sb_2S_3 [46], montmorillonite [47]	Fe_2O_3 [48]
Cationic polyelectrolytes		
Polyethyleneimine	SiO_2 [37], latexes [49]	—
Polyamines	SiO_2 [37], latexes [37]	—
Vinylpyridine-butyl methacrylate copolymers	AgI [50], latexes [51]	—
Poly[dimethyl aminoethylmethacrylate (methyl acrylate)]	Latexes [39, 52]	—

Note. The numbers in square brackets denote refences (Ed. of Translation).

2. Methods of Investigation

The stabilising effect of polymers can be inferred by various methods: from the change in the coagulation thresholds of the sols under the influence of electrolytes determined by measurements of the optical density or light scattering in the system[11,14–20,24,28,33,43,48] or on the basis of direct ultramicroscopic determinations of the number of particles per unit volume,[13,50,51] from the change in the rate of sedimentation of suspensions and of the volume of the deposits,[31,32,34,44,52,53–56] or from the change in the rheological characteristics of the dispersion.[47] Measurements of the dielectric parameters[57] and of the relative electrical conductivities of the dispersions,[58] measurements of light scattering at low angles (below 1°),[59] and laser Doppler spectroscopy[49,60] are promising but as yet little used methods for the study of

the degree of aggregation of particles in disperse systems. A more detailed analysis of the methods for the study of the stability of disperse systems is described in other communications.[8,53]

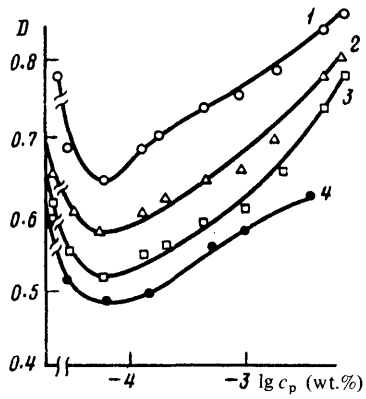

Figure 1. Dependence of the optical density D of a manganite suspension on the concentration c_p of the unhydrolysed (curves *1–3*) and hydrolysed (curve *4*) PAA dispersed in it. Time from onset of precipitation of the dispersion (min): 1) 10; 2) 20; 3) and 4) 30; concentration of the disperse phase $c_{d.p.}$ = 1 g dm^{-3}.[33]

3. The Stabiliser Dose

The processes involving the stabilisation or coagulation of dispersions by high-molecular-weight substances are interrelated. Usually, with increase of the content of the polymer in the system its stability initially falls (flocculation) and the increases (stabilisation). This is illustrated by the variation of the optical density of suspensions of manganite as a function of their content of different polyacrylamide specimens (Fig.1)[33] or by the dependence of the thresholds in the coagulation of silver iodide sol by sodium ions on the concentration of the added poly(ethylene oxide) (Fig.2).[61] Analogous changes in stability have been observed after the addition of poly(vinyl alcohol),[17–20] poly(ethylene oxide),[14–16] and methylcellulose[28] to Au, AgBr, AgI, and Sb_2S_3 sols, of poly(ethylene oxide)[8] and a number of cationic polyelectrolytes[51,52] to a polystyrene latex, of poly(methacrylic acid) to dispersions of a zinc sulphide phosphor,[43,44] etc.

The width of the stabilisation and destabilisation regions depends on a large number of a wide variety of factors: the chemical composition and molecular weight (M) of the reactant, the degree of ionisation of the polyelectrolyte macromolecules, the concentration of the solid phase, the electrolyte content of the system, the duration of contact between the macromolecules and the particles of the disperse phase, and also the method used to estimate the stabilising activity of the HMC. The latter is due to the fact that the vast majority of procedures used to measure the stability are indirect methods sensitive not only to the degree of aggregation of the particles but also to experimental factors, for example, to the wavelength in optical measurements, to the shape of the particles in conductimetric and rheological methods, to the density and type of packing of the particles in the deposits in filtration methods, etc. With the exception of the rapid coagulation thresholds found with the aid of direct ultramicroscopic studies of coagulation kinetics, the threshold in the coagulation of sols by an electrolyte is also a conventional quantity which depends on the duration of the observation and on the composition of the added electrolyte (the thresholds for coagulation by different electrolytes can characterise different degrees of aggregation). In the study of the stabilisation of dispersions by polyelectrolytes one must take into account the influence of the possible chemical interactions of multicharged ions with the functional groups of the stabiliser,[46,62] which alters the coagulation thresholds. It is believed[8] that the "pseudostability" zone observed by Levi and Stepanova[19] before the region of the flocculation of AgBr sols in the presence of PVA and poly(vinyl acetate) is a result of the employment of an unsuitable method for the measurement of the degree of aggregation.

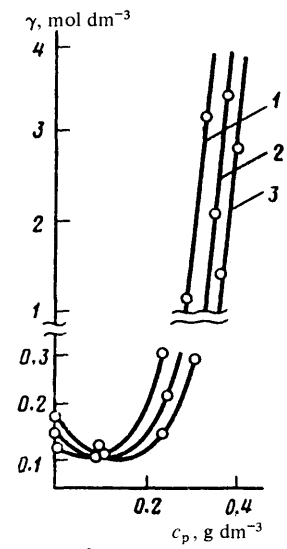

Figure 2. Dependence of the coagulating concentration γ of NaCl for a silver iodide sol on its content of PEO with $M = 1.7 \times 10^4$ and in the presence of different concentrations of KI in the system (mol dm^{-3}): 1) 10^{-2}; 2) 10^{-3}; 3) 10^{-4}; $c_{d.p.}$ = 0.42 g dm^{-3}.[61]

Studies of the influence of the addition of non-ionic polymers (PEO, PVA, and MC) on the stability of hydrophobic gold, silver iodide, antimony sulphide, and polystyrene sols, which was measured in terms of the coagulating concentrations of the counterions, indicate the rules governing the stabilisation of colloidal solutions by uncharged HMC and have much in common:[14–16,18,20,28,61,63] after the attainment of a specific HMC concentration, the dispersion obtains its limiting stability and does not coagulate in the presence of any realistically attainable electrolyte contents in the system: a sharp increase of stability takes place over a narrow range of polymer contents in solution; the thresholds in coagulation by counterions of different charge are gradually levelled out as the concentration of the polymer in the colloidal solution increases; there is a linear relation between the concentration of the solid phase in the sol and the minimum amount of stabiliser necessary for the attainment of a given stability.

Some of these relations are illustrated in Fig.3. The results of adsorption experiments have shown that, in the region of polymer additives corresponding to an abrupt increase of stability, the HMC introduced into the system is wholly absorbed by the disperse phase.[17,28,63-65]

In the studies mentioned above, it has also been shown that small amounts of added non-ionic polymers lower the stability of sols relative to singly charged counterions but not multicharged counterions (see Fig.3); stabilisation takes place only after a fairly broad destabilisation zone. We believe that the appearance of the latter is due to the sensitisation of the system as a result of the interaction of dipolar units of the macromolecule involved in an arrangement of the same type on the opposite walls of the particles. It has been shown theoretically[66] that such interaction leads to the appearance in the system of a negative wedging pressure, i.e. to an additional attraction between the particles. Clearly this mechanism can operate only for low degrees of adsorption of the HMC when the polymer is distributed on the surfaces of the particles in a monomolecular layer and for low values of the "critical gap" between the particles in the coagulation of the sol by singly charged counterions.

When PEO and PVA were added to a sol made up of positively charged AgI particles, an unusual phenomenon was observed—a change in the charge on the particles manifested both by a change in the sign of the electrokinetic potential[67] and by the appearance of a sensitivity of the protected sol to cations,[14] as can be seen from the data in Fig.4. We explained this effect by the occurrence in the oriented layer of adsorbed dipolar segments of the macrmolecules with appreciable "adsorption potential jumps" ψ_a, which are superimposed on the ionic potential of the double layer ψ_i (for $\psi_a > \psi_i$) and can alter the sign of the surface charge of the particle (see also below).

The addition of polyelectrolytes to dispersions sometimes leads to dependences of the stability on the concentration of the reactant more complex than those described above. For example, it has been shown[43,44] that the dependences of the rate of sedimentation and of the optical density of suspensions of the zinc sulphide phosphor on the amount of added poly(methacrylic acid) exhibit a series of minima and maxima (Fig.5); the authors explained this by the simultaneous alteration of the electrokinetic potential of the particles and of the thickness of the adsorption layer with increased degree of adsorption of the stabiliser macromolecules.

4. The Influence of the Molecular Weight

As a rule the stabilising effect of the HMC increases with increase of *M*. In other words, a sharp increase of stability is attained at a lower concentration of the polymer in the system the higher the degree of its polymerisation. This dependence can be clearly traced after the addition of PEO to gold[11-13] and silver iodide[14,15] sols and to polystyrene latex,[8,63] of PVA to silver iodide[17,18] and antimony sulphide[20] sols and an o/w (oil in water) emulsion,[21] of CMC and MC to colloidal AgI and Sb_2S_3 solutions,[28,46] of PAA to kaolinite suspensions,[8] etc.

It has been shown[11,14] that low-molecular-weight specimens of poly(ethylene glycols) ($M < 2 \times 10^3$) do not alter the thresholds in the coagulation of gold and silver iodide sols by an electrolyte. At the same time it has been observed that the variations of the stabilising and flocculating effects of PEO on calcium carbonate suspensions[68] and of the effect of PAA on calcium phosphate dispersions[69] with the molecular weight of the HMC pass through a maximum. After the addition of non-ionic polymers to hydrophobic sols by the "double addition" method (the reactant is added to half the volume of the dispersion and after a time this solution is mixed with a second portion of the initial colloidal solution[12,13,17]), the optimum dose of the flocculant and stabiliser depends little on its molecular weight, which was explained by the weak dependence of the equilibrium thickness of the adsorbed layer of flexible-chain polymers on the degree of their polymerisation. We believe[53] that the different dependences of the flocculating and stabilising effects of polymers on *M* are determined by a series of factors: the degree of approach to the HMC adsorption equilibrium, the dependence of the thickness of the adsorbed polymer layer and of the character of

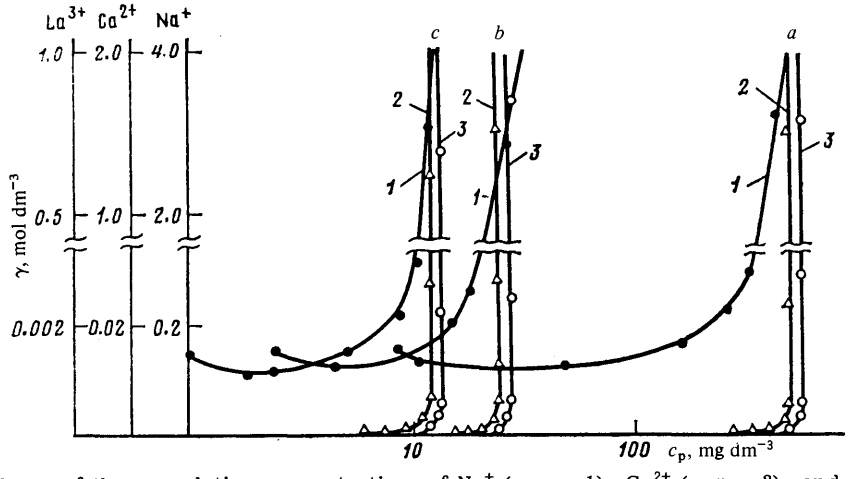

Figure 3. Dependence of the coagulating concentrations of Na^+ (curve *1*), Ca^{2+} (curve *2*), and La^{3+} (curve *3*) ions for an antimony sulphide sol on the content in the system of PEO having different molecular weights: *a*) 2.3×10^5; *b*) 1.3×10^6; *c*) 2.6×10^6.[16]

the distribution in the latter of the macromolecular segments on the degree of polymerisation, and also the mechanism of the stabilisation or flocculation processes.

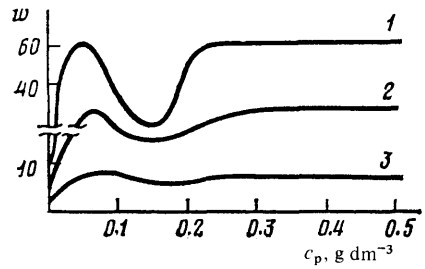

Figure 5. Dependence of the coagulation retardation coefficient w for a suspension of the zinc sulphide phosphor on the content of added poly(methacrylic acid) for different $c_{d.p.}$ (g dm^{-3}): 1) 0.1; 2) 0.25; 3) 2.0.[44]

5. The Influence of the Concentration of the Solid Phase

In most cases it has been observed that the higher the content of the solid phase in the system the higher the HMC concentration at which the same stabilisation effect is attained. For dilute sols, there is a linear relation between the concentration of the disperse phase and the minimum amount of the polymer necessary to attain a specified stability (i.e. approximately equal thresholds in coagulation by an electrolyte).[14-16,18,20,28,62] A similar dependence for the coagulation of AgI and Sb_2S_3 salts containing added poly(ethylene oxide), proportional to the concentration of the solid phase, is illustrated by the data in Table 2..

The above dependence indicates indirectly the complete adsorption of the polymer in the experimental concentration range and shows that, in order to attain a given degree of stabilisation, the same surface coverage of the particles by the high-molecular-weight substance is required. Within the framework of these ideas, the increased stability of AgI sols containing the same amount of added PEO with increase of their age, which we have observed,[61] can be explained by the decrease in the area of the adsorbing surface and by the accompanying increase of the amount of HMC corresponding to a unit surface area.

Table 2. Dependence of the thresholds in the coagulation of AgI and Sb_2S_3 sols by sodium chloride (γ_{NaCl}) on the content of the solid phase in the presence of added poly(ethylene oxide).[16]

$c_{d.p.}$, g dm^{-3}	c_{PEO}, mg dm^{-3} ($M = 1.7 \times 10^4$)	γ_{NaCl}, mmol dm^{-3}	c_{PEO}, mg dm^{-3} ($M = 1.3 \times 10^6$)	γ_{NaCl}, mmol dm^{-3}
		AgI sol		
0.5	3.2	140	1.7	240
1.0	6.4	145	3.4	250
2.0	9.6	140	5.1	250
		Sb_2S_3 sol		
0.2	12.8	60	1.7	350
0.4	25.6	65	3.4	325
0.6	36.4	65	5.1	340

6. The Influence of Particle Size

There are few literatue data concerning the influence of this factor on the conditions in the stabilisation of dispersions by polymers. It has been shown[56] that the form of the influence of the same amounts of added PEO on the rate of sedimentation of silica suspensions (for a constant $c_{d.p.}$) depends on the size of their particles: a gradual stabilisation of the systems has been observed for the coarsest fractions with increase of the HMC concentration, whereas flocculation has been noted for the fine fractions before stabilisation. It has been observed[70] that the flocculating (and stabilising) concentration of polyelectrolytes for fine-particle silica suspensions (particle diameter < 40 mn) is proportional to the specific surface of the particles, i.e. is inversely proportional to their diameter, whereas for large particles it varies

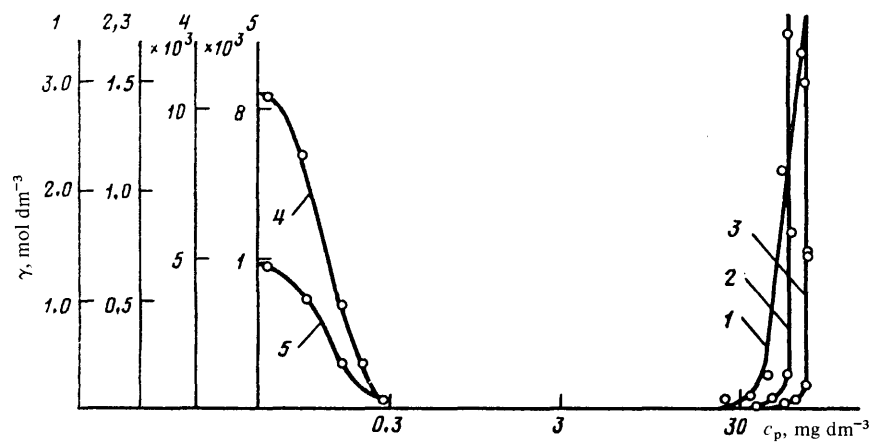

Figure 4. Dependence of the coagulating concentrations of Na^+ (curve 1), Ca^{2+} (curve 2), La^{3+} (curve 3), NO_3^- (curve 4), and SO_4^{2-} (curve 5) ions for a positively charged silver iodide sol on its content of PEO with $M = 2.6 \times 10^6$.[14]

in proportion to the square of the particle diameter. Thus the influence of the particle size on the stabilisation is associated with the variation of the adsorption surface area of the disperse phase. However, here one must also bear in mind the possible influence of the variation of the thickness of the adsorbed polymer layers, for a given specific adsorption, with increasing radius of curvature of the particles.[71]

7. The Influence of Temperature

It has been shown[72,73] that the critical concentrations of the counterions for the Au, AgI, As_2S_3, and Sb_2S_3 sols containing small amounts of added PEO, PEA, CMC, and gelatine diminish significantly with increase of temperature, while in the range 32–40° abrupt changes appear in the $\gamma-T$ curves (Fig.6). For the same sols without polymer additives, anomalous changes in stability with increasing temperature have not been discovered.[74] Therefore the above features of the influence of temperature on the stability can be naturally attributed in the first case to a change in the nature of the surface of the particles as a consequence of the adsorption of hydrophilic substances on the latter. The overall decrease of γ with increase of temperature is caused by the gradual dehydration of the particles and the decrease of the thickness of the lyosphere surrounding them.

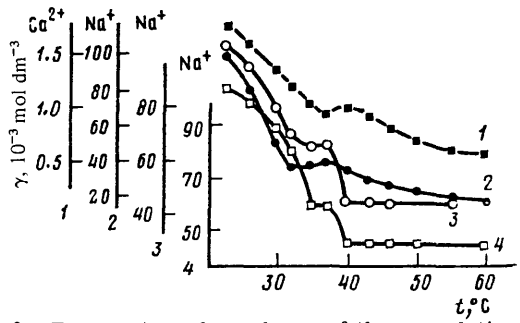

Figure 6. Temperature dependence of the coagulating concentration of the counterions for an antimony sulphide sol when the system contains 9.6 mg dm^{-3} of PEO with $M = 1.7 \times 10^4$ (curve *1*), 20.6 mg dm^{-3} of PEO with $M = 1.1 \times 10^5$ (curve *2*), 7.2 mg dm^{-3} of PEO with $M = 2.6 \times 10^6$ (curve *3*), and 14 mg dm^{-3} of PEO with $M = 1.3 \times 10^6$ (curve *4*).[72]

8. The Influence of the Degree of Surface Coverage

Measurements of the degree of adsorption and of stability carried out on the same object revealed a dependence of the stabilising effect of the HMC on the amount of polymer adsorbed by a unit surface. It has been shown[15,17,18,20,28,56,63] that for each polymer there exists a definite "critical" degree of adsorption Γ_{cr}, the abrupt increase of the stability of the sol being caused by the attainment of this degree of adsorption or its being exceeded (Fig.7); the above degree of absorption usually varies in the range 0.4–1.0 mg m^{-2}. Γ_{cr} depends on the nature and the molecular weight of the polymer, on the charge of the polyelectrolyte macromolecules, and ultimately on the structure of the adsorbed polymer layer on a given surface (see below). For example, it has been shown[15] that an increase of the molecular weight of PEO from 2.3×10^5 to 2.6×10^6 results in a diminution of Γ_{cr} for silver iodide sol particles from 1.0 to 0.5 mg m^{-2}. The increase of the fraction of non-hydrolysed acetate groups in the poly(vinyl alcohol) molecule from 2 to 18% gives rise to a decrease of the degree of surface coverage of the AgI particles, corresponding to a sharp increase of the stability of the sol, from ~0.8 to 0.4 mg m^{-2} (Fig.7).

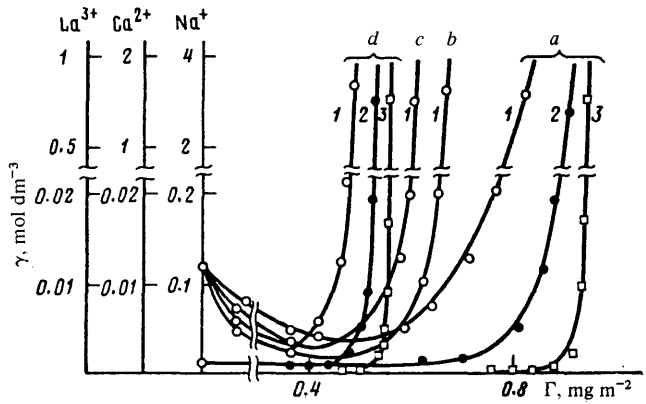

Figure 7. Dependence of the coagulating concentrations of Na^+ (curve *1*), Ca^{2+} (curve *2*), and La^{3+} (curve *3*) ions for a AgI sol on the degree of adsorption of PVA; *a*) $M = 2.2 \times 10^4$, 12% of acetate groups; *b*) $M = 4.1 \times 10^4$, 2% of acetate groups; *c*) $M = 5.9 \times 10^4$, 12% of acetate groups; *d*) $M = 6.5 \times$ *d*) $M = 6.5 \times 10^4$, 18% of acetate groups.[18]

One must note that in a system as complex as a hydrophobic sol–polymer solution–electrolyte solution system an increase of temperature not only disrupts the boundary solvation layers but also alters the solid phase–HMC solution adsorption equilibrium and the conformation of the adsorbed macromolecules and causes a rearrangement of the water structure in the surface hydrate layers. On the basis of general theoretical considerations and the experimental data obtained,[72,73] one can assume that none of the factors enumerated, except the last, can undergo abrupt changes over a narrow temperature range. This is also indicated by numerous data concerning the anomalous changes in many properties of adsorbed water precisely in the temperature range indicated.[75]

However, comparison of the results of the adsorption and coagulation measurements requires caution. This is because measurements of the degree of adsorption of HMC are carried out on colloidal deposits (sol coagulates) and those of stability are performed on "live" dispersions. It may be expected that a smaller surface area is available for the adsorption of macromolecules in the coagulates than in the sols and suspensions owing to the possible aggregation of particles on coagulation. According to Koopal and Lyklema,[76] ~35% of the surface of the particles in silver iodide suspensions and deposits is inaccessible to the adsorption of PVA. As a result of the aggregation of the particles in the presence of the polymer (partial flocculation), the specific adsorption of HMC at a given equilibrium concentration becomes a function of the content of the solid phase in the dispersion, as has been

shown for the adsorption of poly(vinyl alcohol) in suspensions of montmorillonite,[77] silver iodide,[76] and other systems.[78] This is reflected in its turn in the stability of the sol.

It has been observed in a number of studies that the addition of electrolytes decreases the degree of adsorption of non-ionic polymers by the disperse particles[64,65] and increases the degree of adsorption of polyelectrolytes.[79,80] This complicating effect must also be taken into account in devising a relation between the stability and the degree of adsorption of HMC on the basis of the determination of the concentrations of the electrolytes at the coagulation point.

III. THEORETICAL IDEAS CONCERNING THE STABILISATION OF COLLOIDAL SOLUTIONS BY ADSORBED LAYERS OF NON-IONIC POLYMERS

According to modern ideas, the stability of disperse systems is determined by the balance of the attraction and repulsion forces between the particles. In ion-stabilised dispersions, these are van der Waals attraction and repulsion forces in electrical double layers.[1,4] The adsorption of water-soluble polymers by charged particles alters the above forces by changing simultaneously the effective Hamaker constant and the structure of the electrical double layers of the particles. Moreover, the adsorption gives rise to the appearance of additional repulsion forces during the interaction of the adsorbed macromolcules and the appearance (or the enhancement of the role) of the solvation stability factor—the so-called structural component of the wedging pressure.[81] In real disperse systems the above factors are manifested simultaneously, i.e. the stability is determined by the joint action of several of these. Hence it is evident that the theoretical interpretation of the mechanism of the stabilisation of dispersions by high-molecular-weight substances and the search for theoretically well-founded criteria governing the application of a particular HMC for this purpose are complex.

In considering the contribution of the above components to the overall interaction energy of polymer-containing particles (ΔF), it is necessary to bear in mind that the influence of the adsorption of the HMC on ΔF is determined not only by the degree of adsorption of the polymer but also by the structure of the adsorbed layers formed on the surface of the particles—their thickness, the form of the distribution of the density of the segments along the normal to the surface $\rho(x)$, and the number and length of the "tails" and "loops" bound to a unit surface. The determination of these characteristics requires the application of special research techniques[5,6,8,17,63] and some of these, for example, the character of the functions $\rho(x)$, can be estimated only theoretically.[17,82,83]

In this review we are unable to consider the modern ideas about the adsorption of HMC on a solid surface and about the structure of the adsorbed polymer layer; these questions have been discussed in a number of communications.[2,5,6,8,17,82,83] We shall only mention the principal features necessary for the understanding of the problem under consideration.

The structure of the polymer shell on a solid surface depends on many factors—on the amount of the adsorbed substance and its molecular weight, the adsorption energy of an elementary unity, the quality of the solvent, the flexibility of the polymer chain, and, for polyelectrolytes, also the density of the electric charges on the latter. Various models of the adsorbed HMC layers have been discussed and justified: in the form of a thin layer with a large number of contacts between the macromolecule and the surface[84]—this obtains when the affinity of the polymer for the surface is high, i.e. in the presence of chemisorption interactions between the HMC and the adsorbent; in the form of an undeformed polymer coil (when the interaction between the rigid macromolecule and the surface is relatively weak);[28,85] in the form of supermolecular formations transferred to the surface from concentrated HMC solutions;[2,5] in the form of loops and tails of equal or different sizes[6,15,17,18,63–65,76] and (for polyelectrolytes) in the form of ellipsoids of rotation for different degrees of deformation.[79,80]

At the present time the stabilisation of hydrophobic dispersions by the addition of non-ionic flexible-chain water-soluble polymers is most readily susceptible to theoretical interpretation. The adsorption layer is in this case usually described in terms of the Bulas–Hoeve–Hesselink model,[82,86] according to which the polymer shell on the surface consists of a denser first layer (with a relatively large number of contacts between the macromolecule and the surface) and a loose layer made up of unequal tails and loops turned towards the liquid whose distribution with respect to size is described by an exponential relation.[17,82] The density of the segments changes abruptly at the boundary between the first and second layers.[86] Depending on the conditions, linear, power, or most frequently, exponential $\rho(x)$ relations have been postulated for the peripheral part of the adsorbed layer.

We shall consider the influence of the adsorption of polymers on various components of the interaction energy of disperse particles.

1. The van der Waals Attraction

The presence of a surfactant or a polymer around part of the layer can diminish the attraction energy ΔF_A between them both as a result of steric considerations (owing to the increase of the minimum distance to which the particles can approach one another) and because the adsorbed layers alter the effective Hamaker constant A. In the expressions describing the relation between ΔF_A and A (see, for example, Fridrikhsberg[4] and Sonntag and Strenge[88]) the attraction energy is a function not only of the interaction constant of the disperse phase (A_1) and the dispersion medium (A_2) and the constant for the interaction of the disperse phase with the medium (A_{12}) but also of the Hamaker constant of the adsorbed layer (A_3).

The influence of the parameters of the adsorption layers of the polymers on the molecular attraction of the disperse particles has been considered theoretically in a study[89] where the following expression for ΔF_A was obtained in the case of unretarded London forces in terms of the microscopic approximation:

$$\Delta F_A = -\frac{1}{12}\left[(A_2^{1/2} - A_3^{1/2})\frac{a+h}{a-2h} + (A_3^{1/2} - A_1^{1/2})\frac{a}{d} + 4(A_2^{1/4} - A_3^{1/4})(A_3^{1/4} - A_1^{1/4})\frac{a+h}{(d-h)(2+h/a)}\right] \quad (1)$$

where a is the radius of the particles, d the distance between them, and h the thickness of the adsorbed HMC layer.

Vincent[90] derived the corresponding equations for retarded London forces and also examined the case of the interaction between plates and a sphere containing a homogeneous adsorbed layer on the surface. Some of his results are illustrated in Fig.8. Deryagin and Churaev[81] and Ninham and Parsegian[92] obtained an analytical expression for the London–van der Waals forces in the case of three-layer films in air and in water on the basis of the macroscopic Lifshits theory of interactions between condensed bodies.

The complex expressions obtained for ΔF_A can be simplified under certain conditions. For example, for emulsions of the water/oil type stabilised by hydrocarbons, one can assume that $A_2 \cong A_3$, since the molecular interaction forces between hydrocarbon chains and between the latter and the oil are similar.[88] In the general case the adsorption of polymers can both diminish and increase the attraction between the particles. Its influence is determined by the results of the combination of Hamaker constants: when a dense particle ($A_1 > A_2$) is "clad" in a light adsorbed layer ($A_3 < A_2$), the effective Hamaker constant for the particle plus adsorbed layer system decreases. Conversely, a heavy coat with a low density diminishes the attraction. However, it has been shown[89] that the change in A owing to the appearance of adsorbed polymer layers never converts attraction into repulsion.

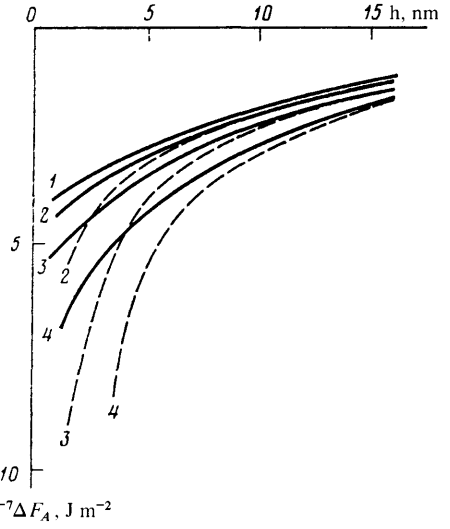

Figure 8. Theoretical variation of the influence of the adsorbed homopolymer on the van der Waals attraction of two plane-parallel plates on the assumption of an exponential (continuous lines) or uniform (dashed lines) distribution of the density of units in the adsorption layer. Average volume fraction of units in the layer: *1*) 0; *2*) 0.03; *3*) 0.1; *4*) 0.2. The Hamaker constant is $20kT$ for the particles, $17.5kT$ for the polymer, and $10kT$ for the solvent; the thickness of the layer is 10 nm.[90]

The influence of the Hamaker constant for the adsorbed layer A_3 on the particle attraction force has been examined[93] and it has been shown that, under the conditions where $A_1 > A_2$, the plot of ΔF_A against A_3 passes through a minimum. In discussing the influence of the adsorption of water-soluble polymers on A, one must bear in mind that the adsorbed layer contains polymer units plus water molecules. According to Fleer and Lyklema[55] and Sonntag and Strenge,[88] when the polymer is strongly hydrated one can assume that $A_2 \cong A_3$, i.e. that the molecular attraction of the particles with the adsorbed layer is the same as the attraction in the pure dispersion medium. In this case the expression for the attraction energy becomes

$$\Delta F_A = -\frac{1}{12}(A_2^{1/2} - A_1^{1/2})^2 \frac{a}{d}. \qquad (2)$$

The character of the distribution of the density of the units in the adsorbed layer influences significantly the $\Delta F_A(A)$ relation, primarily over short interparticle distances.[90,93]

New possibilities for a more exact calculation of the influence of the adsorption of HMC on the molecular attraction of the particles have been provided by Lifshit's macroscopic theory. Without going into the description of this theory here (see, for example, Dzyaloshinskii et al.[94]), we may note that the results of the calculation of ΔF_A by the Lifshits method, particularly for aqueous media, can differ markedly from those based on the London theory,[8,95] because the high polarity of water leads to a greater contribution to A by polarisation interactions at infrared and microwave frequencies than at ultraviolet frequencies (in Hamaker's procedure only the ultraviolet frequencies of the dispersion are used in the calculations of A). Furthermore, allowance for the low-frequency components of the distortion forces in the macroscopic theory leads to a dependence of A on temperature[91,92] and on the presence of salts in the system. All these factors must be considered in discussing the influence of the adsorption of HMC on the molecular attraction of the particles.

2. The Repulsion of Electrical Double Layers

The adsorption of non-ionic polymer macromolecules can alter the parameters of the electrical double layer, which is reflected in its turn in the contribution of the electrical component ΔF_R to the particle interaction energy. These changes reduce mainly to the following.

(a) The accumulation of polymer units in the Stern layer can alter the density of the electrical charges on the surface—either as a result of a change in the dielectric constant and hence of the capacity of the double layer or as a result of the appearance of "adsorption potential jumps" ψ_a in the oriented layer of dipolar segments on the surface. The appearance of ψ_a having the same sign as the ionic potential jump ψ_i, under the conditions of a constant interphase potential jump ($\psi_0 = \psi_i + \psi_a$), inevitably entails a decrease of ψ_i (subject to the condition $\psi_a < \psi_i$) or even alters its sign (when $\psi_a > \psi_i$), which is manifested experimentally as a change in the charge on the particles in the presence of the added non-ionic polymer.[14,63,67]

(b) The adsorbed macromolecules can displace from the Stern layer some of the specifically adsorbed counterions, which increases the ψ_1 potential and hence the stability of the colloidal solution. This explains, for example, the initial increase in the electrokinetic potential of AgI particles in the presence of small amounts of added poly(ethylene oxide)[67] or poly(ethylene glycol).[96]

(c) The formation on the surface of a fairly dense adsorbed polymer layer with a high density of units, in which water loses its solvent power, leads to an increase in the thickness of the Stern layer and to the separation of the components of the double layer, which is again responsible for the growth of the ψ_1 and ζ potentials,[97] i.e. for the stabilisation of the dispersion. These ideas have been evoked to account for the increased stability of hydrophobic sols as a result of the adsorption of diphilic molecules of organic substances[98,99] and can also be used to interpret a wide variety of changes in the stability of disperse systems in the presence of polymeric additives.[8,44]

(d) The formation on the surface of fairly thick hydrodynamically impermeable layers of non-ionic polymers shifts the slip planes into the bulk of the liquid phase, which entails a decrease in the ζ potential and in the contribution of the electrical forces to the repulsion of the polymer-containing particles. These ideas have served as a basis for calculating the effective thickness of the adsorbed layers of non-ionic HMC (for a more detailed description, see Refs.6, 9, and 17).

The addition of oppositely charged polyelectrolytes to a colloidal solution usually leads to a significant decrease in the ζ potential and to a change in the charge of the particles,[48,50-52] which is accompanied by the destabilisation (flocculation) of the system. As a rule, the stability minimum and the isoelectric point of the particles of the dispersion do not coincide.[48,50-53,100] The adsorption of polyelectrolytes bearing charges of the same kind as the particles is in many cases responsible for the increase in the electrokinetic potential and for the stability of the dispersion.[44,46,52,63]

3. Interaction of the Adsorbed Macromolecules

The adsorbed macromolecules are hardly ever located in a planar position on the surface: some of the macrochains in the form of loops and tails are immersed in the surrounding liquid. The interpenetration of two such adsorbed layers gives rise to repulsion forces of two types:[8,101] (1) as a consequence of the decreased number of possible conformations of the polymer chain, which leads to the loss (decrease) of the configurational entropy and hence to an increase in the free energy of the system and (2) owing to a change in the polymer–solvent interaction in the overlap zone and the appearance of a local osmotic pressure under these conditions. In a details study it is possible to differentiate two limiting cases of the "entropic repulsion".[8,101] The first arises when the decrease of the entropy of the system in the interaction of adsorbed molecules entails desorption of the latter. This increases the interfacial free energy, i.e. leads to the repulsion of the particles. This model has been considered theoretically[102,103] in relation to short weakly adsorbable rod-like molecules, which have sufficient time for desorption during the elementary particle collision step. It explains, for example, the stabilisation of dispersions of carbon black in hydrocarbons by alkylbenzenes,[104] the extremum in the dependence of the stabilising effect on the degree of surface coverage by the polymer,[103] etc. For slowly desorbable or altogether non-desorbable high-molecular-weight polymers (i.e. when the simultaneous rupture of a large number of contacts with the surface is unlikely), another mechanism is more suitable, in which it is assumed that, in the course of particle collisions, the polymer–particle adsorption equilibrium does not change and the increased free energy of the system is due to the decrease of its entropy following the redistribution or compression of the adsorbed segments in the overlap zone.

In this constant adsorption model one distinguishes in its turn two limiting cases: the mutual interpenetration of the adsorbed layers without the compression of the adsorbed polymer chains (the "mixing" effect) and compression of the adsorbed layers without their mutual overlapping (the "volume restriction" effect). Naturally both these cases are idealised and there are always difficulties in selecting a model of the interaction in quantitative calculations, because the two contributions mentioned above cannot be separated in real systems. On the basis of general considerations, one can only assume that at a high concentration of units on the surface, in the adsorption of substances with not unduly high molecular weight and when the interacting surfaces have approached one another very closely, the "volume restriction effect" will predominate, while for low degrees of surface coverage, for low degrees of adsorption of low-molecular-weight polymers, and for large interparticle distances, the "mixing" effect is the dominant one.[8,15] Difficulties also arise in the selection of a model of the adsorbed layer in the form of tails or loops. The distribution of the density of units in the loop and in the tail, which determines the interaction between the macromolecules, changes in different ways with increasing distance.[105-107] It has been shown theoretically that in the case of a long-chain homopolymer it is possible to neglect the concentration of the tails compared with that of the loops,[82] but for not an unduly long macromolecule the adsorption in the form of tails is energetically more favourable.

A number of attempts have been made at a quantitative calculation of the repulsion energy of hypothetical particles (plates) with a polymer coating, caused by the "volume restriction" effect (ΔF_{VR}) and the "mixing" effect (ΔF_M). ΔF_{VR} has been calculated[102] for short rigid rodlike molecules on the hypothesis that the increase in the free energy of the system is determined by the decrease of the configurational entropy S as the second surface approaches: $S = k \ln N$ (where N is assumed to be proportional to the area occupied by the free ends of the rods). Mackor's model has been extended[108] to the interaction of a sphere with another sphere, the lateral interaction of the adsorbed chains being considered simultaneously. Using the same concentration, an increase in the entropic repulsion with increasing length of the macromolecular chain, the impossibility of stabilisation of unduly small particles by macromolecules having the specified lengths, etc. have been predicted theoretically.[109] The earlier attempts to calculate ΔF_{VR} are not considered here, since they were based, as shown by Hesselink,[106] on an incorrectly selected distribution of the densities of the adsorbed units as a function of the distance from the surface; furthermore, they have been considered in fair detail in another review.[8]

The "mixing" or osmotic effect was first considered by Fischer.[110] In the derivation of an expression for the calculation of the contribution ΔF_M, arising when two spherical polymer-containing particles approach one another, he suggested that (1) the concentration of the segments in the adsorbed layer is identical throughout, (2) the concentration of the segments in the overlap region is equal to the sum of the concentrations in both interacting adsorbed layers, and (3) that the Flory–Krigbaum theory of dilute solution is applicable to the calculations of ΔF_M. In this theory the free energy of mixing of the polymer units and solvent molecules in a small volume element is expressed as:[111]

$$\delta(\Delta F_M) = kT(\delta n_1 \ln \Phi_1 + \chi \delta n_1 \Phi_2), \qquad (3)$$

where δn_1 is the number of solvent molecules in the volume element δV, Φ_1 and Φ_2 are the volume fractions of the solvent and the polymer respectively, and χ is the Flory–Huggins interaction parameter. The change in the free energy of mixing in the volume V is calculated as the sum of the changes in all the volume elements. Thus an expression has been obtained[110] for calculating the repulsion energy between two particles with an adsorbed layer of a non-ionic polymer:

$$\Delta F_M = \frac{4\pi k T c^2}{3 V_1 \rho^2} (\psi - \chi) \left(h - \frac{d}{2}\right)^2 \left(3a + 2h + \frac{d}{2}\right) \qquad (4)$$

where c is the concentration of the polymer segments per unit volume of the adsorbed layer, ρ the density of the adsorbed

substance, h the thickness of the layer, V_1 the partial molar volume of the solvent, and ψ the entropic parameter of the interaction.

For small overlaps, the hypothesis (2) is entirely reasonable, but for larger overlaps it is not very suitable. It follows from the work of Hesselink[106] that the first assumption also has little justification in this theory. An advantage of Meier's theory[109] is the use in the expression for ΔF_M of the familiar Flory parameter χ in an explicit form, which makes it possible to take into account the contribution of the nature of the solvent to the repulsion. On the other hand, the expression for $\rho(x)$ used by the same investigator is apparently erroneous.[8,106]

The latest advances in this field are associated with the development of statistical methods for the calculation of the number of conformations of adsorbed macromolecules by Hesselink[82,106] and other workers.[112,113] Hesselink[106] quotes an expression for the calculation of the number of conformations of a single loop and a single tail lost following the approach of a second surface, subject to an exponential distribution of the density of units along the normal to the surface. On this basis, Hesselink et al.[114] derived relations suitable for the calculation of the increase in the free energy of the system resulting from the restriction of the volume of the adsorbed polymer chains and their mixing (calculated per unit area of the surface):

$$\Delta F_{VR}=2\nu kTV(\bar{i}, d); \quad (5)$$

$$\Delta F_M=2(2\pi/9)^{3/2}(\alpha^2-1)kT\nu^2\langle r^2\rangle M(\bar{i}, d). \quad (6)$$

In these expressions the terms $V(\bar{i}, d)$ and $M(\bar{i}, d)$ describe the increase in the free energy as a function of the distance d between the surfaces for the average loop; they depend on the mechanism of binding of the macromolecule to the surface and on the average number of units in the loop $\bar{i}$; ν is the number of loops (tails) per unit area, α the swelling coefficient, and $\langle r^2\rangle^{1/2}$ the mean square distance between the ends of the polymer chain.

Relations for the calculation of $V(\bar{i}, d)$ and $M(\bar{i}, d)$ have been published.[114] Various cases of the binding of macromolecules to the surface were then considered, namely adsorption in the form of tails and loops of equal size, in the form of a macromolecule with an exponential distribution of tails and loops with respect to size, or in the form of a homopolymer all the segments of which have equal chances of binding to the surface.

The values of $V(i, d)$ and $M(i, d)$ for a simplified model, frequently used in practice, of the adsorption of a polymer in the form of identical loops and subject to the conditions $d/(il^2)^{1/2} \geq 1$ can be calculated from the following relations with an error up to 2%:[114]

$$V(i, d)=-2(1-12d^2/il^2)\exp(-6d^2/il^2), \quad (7)$$

$$M(i, d)=(3\pi)^{1/2}\{6d^2/il^2-1\}\exp(-3d^2/il^2), \quad (8)$$

where i is the number of units in the loop.

Although the Hesselink–Vrij–Overbeek (HVO) theory yields reasonable values for ΔF_{VR} and ΔF_M and can, as will be shown below, predict many experimental relations, it has a series of weak points. Since it uses the exponential distribution $\rho(x)$, it assumes the existence of the "volume restriction" effect over any interparticle distances, which is naturally incorrect. Nor is the hypothesis that the values of α for macromolecules in the bulk phase and in the adsorbed layer are identical fully justified in the HVO theory. In addition, it suffers from the limitations of the Flory–Krigbaum theory, which constitutes the basis of the calculation of ΔF_M.

The Napper–Evans steric stabilisation theory[115–119] constitutes an expansion and development of the Fischer theory. The main factor determining the stabilisation of HMC dispersions is believed by these authors to be the polymer–solvent interaction, which influences decisively the conformation of the stabiliser in the surface layer of particles. A satisfactory stabilisation is attained when the solvent used is better than a θ-solvent; under these conditions, the polymer–solvent interaction predominates over the polymer–polymer and solvent–solvent interactions. Near the θ-point a transition should be observed from a stable to an unstable state, as follows from Eqn.(4), according to which $\Delta F_M = 0$ under θ-conditions, where $\chi = 0.5$. On passing to solvents inferior to the θ-solvent, the medium–medium and polymer–polymer interactions become energetically more favourable ($\Delta F_M < 0$), which leads to flocculation in the system. Conversely, positive values of ΔF_M ensure the stabilisation of the system.

Numerous experiments whereby Napper and co-workers[115–119] did indeed demonstrate convincingly that, after the attainment of θ-conditions (by altering the temperature or solvent composition), there is an abrupt change in the stability of polymer dispersions stabilised by various block copolymers of type AB. Analysis of stabilisation conditions[118] for ~40 systems has shown that the θ-point is close to the limit of stability of a sterically protected dispersion and that the θ-point and the critical point for flocculation are clearly correlated in both aqueous and non-aqueous media.

Napper introduced the concept of the enthalpic, entropic, and mixed entropic-enthalpic stabilisations. This classification is best examined by dividing the free energy change occurring on mutual interpenetration of the macromolecular chains (the energy of mixing) into the enthalpic (ΔH_M) and entropy (ΔS_M) components:

$$\Delta F_M=\Delta H_M-T\Delta S_M. \quad (9)$$

The generalised Flory–Huggins interaction parameter, characterising the thermodynamics of the polymer–solvent interaction, can be represented in its turn by the sum

$$\chi=\chi_h+\chi_s,$$

where χ_h is the parameter of the enthalpy of mixing (measured calorimetrically) and χ_S is the entropic parameter, which characterises the volume effects of mixing, a change in the structure, dissociation and formation of hydrogen bonds, etc. At infinite dilution, $\Delta H_M \to (-q)$ and $\Delta H_S \to (-\psi)$, where $q = \chi_h$ and $\psi = 1/2 - \chi_S$. On the basis of the above considerations, Napper[120] established the conditions under which a particular type of steric stabilisation predominates (Table 3).

Table 3. Comparison of different types of steric stabilisation (according to Napper).

q	ψ	ΔH_M	ΔS_M	$\Delta H_M/\Delta S_M$	ΔF_M	Type of stabilisation
<0	<0	>0	>0	>1	>0	Enthalpic
>0	>0	<0	<0	<1	>0	Entropic
>0	<0	<0	>0	≷1	>0	Mixed

The majority of solutions of polymers in non-polar media are characterised by positive values of q and ψ and therefore entropic stabilisation is to be expected for them. Negative

values of q and ψ, caused by the rupture of the hydrogen bonds with increased HMC concentration in the system, correspond to many polymers in non-aqueous solutions (for example, a solution of PEO in water). The addition of dioxan to aqueous solutions of surfactants decreases the negative (increases the positive) values of q and ψ, which is accompanied by a transition from the enthalpic to the entropic mechanism of stabilisation.[120]

The type of steric stabilisation can be established from the form of the change in the disperse system with increase of temperature. Napper and co-workers showed[117–119] that colloidal systems, which flocculate on aggregation, undergo enthalpic stabilisation at least below the critical flocculation temperature (c.f.t.), while systems which flocculate on cooling are stabilised entropically at least above the c.f.t. In other words, systems with enthalpic stabilisation tend to lose stability on heating, while entropically stabilised systems flocculate on cooling. According to Napper,[117] the c.f.t. is the minimum temperature causing the flocculation of dispersions stabilised enthalpically or the maximum temperature at which dispersions stabilised entropically flocculate.

A new approach to the problem of the stabilisation of colloids by non-ionic polymers has been developed recently in a study[121] whose authors attribute the appearance of repulsion forces to the presence in the solution of free non-adsorbable HMC. Such a situation can obtain for an inert surface or a surface which repels the polymer and also when all the adsorption centres on the surface have been occupied. The average density of units is assumed to be lower on the surface than in the bulk phase. The appearance of repulsion forces as the surfaces approach one another to distances less than twice the distance between the centres of mass of the macromolecules is attributed to the differences between the free energies of mixing of the polymer with the solvent (calculated by the Flory–Krigbaum procedure) in the initial and final states of the system.

4. Solvation of the Disperse Phase

The adsorption by colloidal particles of water-soluble polymers containing a large number of hydrophilic groups must lead to the hydrophilisation of the surface of the disperse phase and hence to an increased contribution by the solvation stability factors. However, among various aspects of the influence of HMC on the stability of colloidal solutions, this effect has not so far been examined.

Here one should note that the concept of the solvation of the disperse phase as an aggregative stability factor for colloidal systems has been firmly and for a long time incorporated in the literature,[122,123] although neither the structure of the surface solvate layers nor the physical nature of the corresponding repulsion forces have so far been unambiguously established.[124–128] It is believed that the solvation stability factor is determined by the presence on the surface of polymolecular layers of the solvent with an unusual structure (differing from that in the bulk phase) and properties.[124,126–128] The interaction of these layers induces the appearance between them of repulsion forces whose nature has not been finally elucidated. It is most likely that they are caused by a change in the statistical distribution of the water molecules in the overlap zone (by an increase of the degree of their order).[72] The present state of the theory of the liquid state does not permit the calculation of the above forces; they can be estimated only indirectly by subtracting from the experimental force of the interaction of the disperse phases the sums of the theoretically calculated repulsion forces of the double layer and molecular attraction forces.[81] Such estimates have so far been made only for a small number of model systems.[81,129]

The solvation of the disperse phase has been regarded as an important or dominant factor in the stabilisation of not only hydrophilic sols[122,130,131] but also of hydrophobic systems stabilised (hydrophilised) by adsorption layers of low-molecular-weight surfactants.[132,133]

The important role of the structural component of the wedging pressure in the mechanism of the stabilisation of colloidal solutions with a polymer additive is also indicated by data concerning the hydrophilic properties of the stabilised macromolecules as well as the temperature dependence of the stability of polymer-containing dispersions (see Section II). It has been shown[134–136] with the aid of high-resolution NMR and the spin-echo method that three forms of water exist in the PEO–water, PVA–water, and CMC–water systems: the hydration sphere bound firmly to macromolecules and consisting of 2–3 H_2O molecules per unit at the boundary of which there is an abrupt change in many properties of water, the polymolecular hydration layer made up of 16–20 water molecules per unit in which the mobility of water molecules still differs from that in the pure liquid with a gradual transition to the properties of the latter in the bulk phase, and finally water corresponding to the usual liquid in all its properties. Thus, like hydrophilic solid surfaces,[124–128] water-soluble polymers exert a structure-forming effect on several molecular layers of water.

The observed[72,73] abrupt changes in the coagulation thresholds of hydrophobic sols containing water-soluble polymers with increasing temperature can be explained by the influence on the stability by the structural component of the wedging pressure, in particular the structure of water itself in the polymolecular hydrate layers formed on the surface (see Section II). The contribution of this stabilisation factor depends on the degree of adsorption of the HMC by the particles, the degree of hydration of the stabiliser macromolecule, and other factors (see below).

IV. THE MECHANISM OF THE STABILISATION OF REAL DISPERSIONS BY NON-IONIC POLYMERS

It is possible to use two procedures to carry out an experimental test of the theories of the interaction of adsorbed macromolecules and to discover the mechanism of the stabilisation of real HMC dispersions. The first more direct method involves the direct measurement of the repulsion forces of the adsorbed polymer chains and their comparison with the corresponding values calculated theoretically. The second method consists in comparing the experimental characteristics of the stabilisation of dispersions by polymers [the influence on the latter of the degree of adsorption and the molecular weight (MW) of the stabiliser, the ionic strength of the solution, and other factors] with the characteristics predicted on the basis of the analysis of the potential curves for the interaction of polymer-containing particles constructed using the parameters of the electrical double layer and the adsorbed polymer layer, which have been determined by an independent method and which enter into the equations of a particular theory.

1. The Energies of the Interaction of the Particles with the Adsorbed HMC

It follows from the foregoing features described in the previous Section that the overall free energy of the polymer-containing particles is in the general case given by

$$\Delta F = \Delta F_A + \Delta F_R + \Delta F_P + \Delta F_{st} \quad (10)$$

where F_{st} is the contribution of the structural component of the wedging pressure, which cannot be determined quantitatively but which can be neglected, as will be shown below, for high degrees of adsorption of the polymer and $\Delta F_P = \Delta F_{VR} + \Delta F_M$.

Our previous communications[15,16,18,20,22,28,63] present the results of calculation of the component (and their sum) of the interaction energies of silver iodide, antimony sulphide, and styrene particles as well as oil drops in water containing adsorbed PVA, PEO, and MC, using the parameters of the electrical double layer and the adsorbed polymer layer found by independent methods.

The contributions ΔF_{VR} and ΔF_M were calculated from the formulae of the Hesselink–Vrij–Overbeek theory [Eqns.(5) and (6)] for models of the binding of macromolecules to the surface which were most appropriate for a given system: for undeformed statistical coils, i.e. $\langle r^2 \rangle = il^2$ and $\nu = \Gamma N_A/M$, where Γ is the degree of adsorption in g m^{-2} and N_A the Avogadro number (this model is suitable for the adsorption of PVA on the surface of oil in water and of MC on AgI and Sb_2S_3 particles), for loops of equal size, i.e. under conditions where Eqns.(7) and (8) are valid, and, finally, for an adsorbed layer with an exponential distribution of loops with respect to size (the model of adsorbed layers of PVA and PEO on the surface of hydrophobic Sb_2S_3 and AgI particles). For the last two models, the number of loops was found from the relations $\nu = n/\bar{i}$, where n is the number of units in the form of loops bound per unit surface, calculated as the difference between the total degree of adsorption and the degree of adsorption in the first layer. The quantity $\langle r^2 \rangle$ for adsorbed chains was found as $\langle r^2 \rangle = \alpha \bar{i} l^2$, using the quantities $\bar{i}$, l, and α found previously.[6,28,63-65] In conformity with Hesselink's procedure,[82] the concentration of tails compared with that of the loops was neglected for the high-molecular-weight polymers employed.

The attraction energy was found in terms of the microscopic approximation for the model of plane-parallel plates:[88]

$$\Delta F_A = -\frac{A_{12}}{12\pi d^2}. \quad (11)$$

The repulsion energy of the double layer of plates was found from the formula valid when $\kappa d > 1$:[1]

$$\Delta F_R = \frac{\varkappa}{z^2} f(Z); \quad Z = ze\psi_1/kT \quad (12)$$

where z is the charge of the counterion and κ^{-1} the Debye radius.

The Stern potentials ψ_1 for silver iodide and polystyrene particles were determined from the results of dielectric and conductimetric measurements[63] and the surface potential ψ_0, calculated from the charge densities on the surface,[63] was adopted as the effective potential of the Sb_2S_3 particles. The values of the functions $f(Z)$ were taken from the Tables quoted in Kruyt's monograph.[1]

Analysis of the character of the variation of ΔF_{VR} and ΔF_M as a function of the interparticle distance for AgI, Sb_2S_3, or polystyrene containing different amounts of an adsorbed HMC (for example, see Fig.9) leads to the following conclusions.[15,16,18,20,22] Repulsion owing to the overlap and mixing of the adsorbed macrochains is manifested over longer distances than the repulsion induced by the restriction of their volume. This is due to the fact that the former effect arises as soon as the interpenetration of the segments located on the opposite walls begins, while the manifestation of the latter effect (the compression of the flexible polymer chain) requires an adequate approach to the second (restricting) surface.

ΔF_{VR} and ΔF_M increase both with increasing degree of adsorption of the polymer (as a consequence of the lengthening of the adsorbed tails and loops) and as the surfaces approach one another (owing to the involvement in the interaction both of an increasing number of units of the given loop and also of shorter loops). The contribution of osmotic effects is greater in the adsorption of methylcellulose and poly(ethylene oxide) than in the adsorption of poly(vinyl alcohol), because water is a better solvent for the former polymers ($\Delta F_M \propto \alpha^2$). Calculations have also shown that the repulsion of the adsorbed macromolecules increases with increasing molecular weight of the polymer for the same degree of adsorption and the same ionic strength of the solution, despite the fact that the area of the polymer shell is the same under these condition. This is caused by the unequal concentrations of the loops in the adsorbed layer for specimens having different molecular weights. Thus the HVO theory explains the experimentally observed increase of the stabilising effect of polymers with increase of their molecular weight.

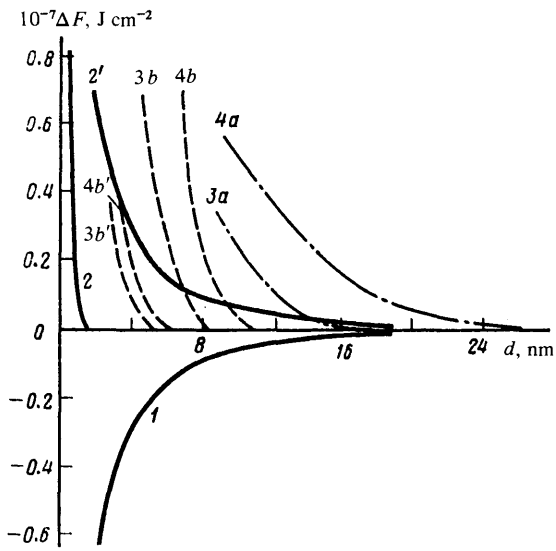

Figure 9. Different components of the interaction energy of Sb_2S_3 particles which have adsorbed 0.4 mg m^{-2} (b') and 1.0 mg m^{-2} (a and b) of PVA with $M = 2.2 \times 10^4$: 1) ΔF_A; 2) ΔF_R in 1 M KCl solution; 2′) ΔF_R in 10^{-3} M KCl solution; 3) ΔF_{VR}; 4) ΔF_M for the model involving adsorption in the form of undeformed coils (a) and with an exponential distribution of loops with respect to size (b).[20]

Comparison of the values of ΔF_R and ΔF_P made it also possible to estimate the contributions of different forces to the repulsion of real particles containing adsorbed HMC. Fig.9 shows that in a concentrated electrolyte solution the stabilisation of the sol is determined in all cases soley by the polymer component, because the double layer is in this case "hidden" within the polymer shell. On the other hand, in the case of dilute electrolyte solutions the contributions ΔF_R and ΔF_P to the repulsion of particles depend on the degree of adsorption of the HMC: with decrease in the salt concentration (with increased thickness of the double layer) and

with decrease of Γ (with a decrease in the length of the loops), the contribution of the repulsion also increases (Fig.10).

Thus the interaction between particles coated by an adsorbed layer of a HMC is not determined solely by the balance of the van der Waals attraction and repulsion forces of the polymer chbins, as has been frequently suggested.[8,107-110,114,121] As a special case, this obtains only in concentrated electrolyte solutions when the thickness of the electrical double layer is much smaller than the effective thickness of the polymer coating; when $\kappa^{-1} > h$, the opposite picture is observed.

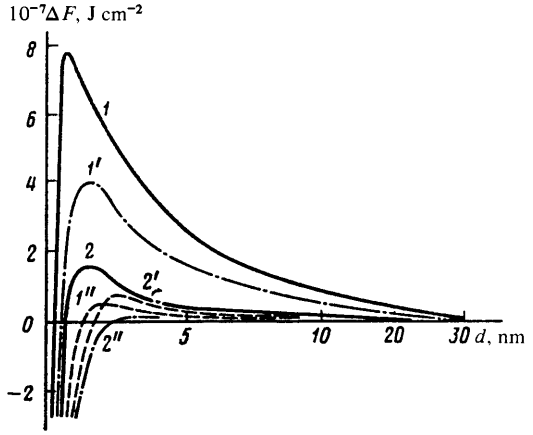

Figure 10. Potential curves for the interaction of Sb_2S_3 particles which have adsorbed 0.4 mg m^{-2} (curves *2*, *2′*, and *2″*) and 1.0 mg m^{-2} (curves *1*, *1′*, and *1″*) of PVA with $M = 2.2 \times 10^4$: 1) and 2) $\Delta F = \Delta F_A + \Delta F_R + \Delta F_{VR} + \Delta F_M$; 1′) and 2′) $\Delta F = \Delta F_A + \Delta F_R + \Delta F_M$; 1″) and 2″) $\Delta F = \Delta F_A + \Delta F_R + \Delta F_{VR}$.[20]

The potential curves for the interaction of the particles with the adsorbed non-ionic polymer have been constructed by adding together ΔF_A, ΔF_R, and ΔF_P.[15,16,18,20,28,63] It has been shown (Fig.10) that, with increase in the degree of adsorption of the HMC, the interaction energy between the particles increases significantly, reaching values amounting to several and several tends of erg cm^{-2}, which explains the formation of highly stable sols in the presence of the PVA, PEO, and MC polymers. Comparison of the results of theoretical calculations by the HVO method with the experimental stabilisation data (see Section II) has shown that the abrupt increase in the stability of the sols occurs for approximately the same degrees of adsorption ($\geqslant$0.5–0.7 mg m^{-2}) as in the case where there is an appreciable barrier preventing the mutual approach of the particles, sufficient for the stabilisation of the colloidal solution. The HVO theory also predicts correctly the dependence of the stabilising effect of polymers on their molecular weight. At the same time this theory in its pure form is unsuitable for the description of the stabilisation of dispersions by the addition of HMC in dilute electrolyte solutions; it does not take into account the change in the interaction of the polymer with the solvent following adsorption and does not allow the separation of the contributions to the interaction caused by the volume restriction and osmotic effects.

Thus, on the basis of the general approach of the physical Deryagin–Landau–Verwey–Overbeek theory of stability (involving the allowance for the balance of the attraction and repulsion forces between the particles) and resorting to the HVO theory, it is possible to interpret many experimental relations obtained in the study of the stabilisation of dispersions by the addition of non-ionic water-soluble polymers and also to determine the contributions of different factors to the stabilisation of these systems.

As already stated, the contribution of the solvation of the particles to the mechanism of the stabilisation of polymer-containing dispersions cannot as yet be estimated quantitatively. However, the set of experimental stabilisation data and their comparison with the results of adsorption measurements permit qualitative estimations. Apparently, in the case of dispersions with a small amount of added polymer, i.e. for small thicknesses of the adsorbed HMC layer, the contribution of the structural component of the wedging pressure is comparable to that of the other stabilisation factors. This is indicated particularly by the results of the study of the temperature dependence of the stability of polymer-containing hydrophobic sols (see Section II). At the same time, in the presence of large amounts of the high-molecular-weight substance in the system, whereupon there is a sharp increase of its stability, the solvation of the disperse phase is a weaker stabilisation factor than the steric repulsion. This is indicated, for example, by the insensitivity to the temperature factor of highly stable polymer-containing sols and the impossibility of achieving their coagulation by adding concentrated salt solutions. This constitutes the radical difference between colloidal solutions protected by low-molecular-weight surfactants, on the one hand, and those protected by water-soluble polymers, on the other. In the former case, the breakdown of the boundary solvate layers (by the addition of dehydrating agents, by an increase of temperature, etc.) leads to the coagulation of the sol[132,133] while in the latter case the same result is not attained.

2. Direct Measurements of the Repulsion Forces Between Adsorbed HMC

The small number of publications on the direct measurement of the repulsion forces between adsorbed macromolecules reflects the difficulty of the experimental study of these systems. Thin aqueous films stabilised by the adsorbed layer of HMC, whose thickness can be measured fairly accurately by optical methods, are convenient objects for study. Furthermore, by altering the hydrostatic pressure, it is possible to determine the dependence of the interaction force between the surfaces (and of its individual components when the remaining components are either constant or small) on the thickness of the gaps separating them. Here it is appropraite to mention that the dependence on interparticle distance of the ionic-electrostatic forces, arising following the overlap of the double layers, was established for the first time precisely in relation to liquid films and the principal conclusions of the DLVO theory were subjected to a quantitative test.[88,137]

The condition for equilibrium in the liquid film is defined thus:[88]

$$P_A + P_R + P_P + P_h = 0 \qquad (13)$$

where P_A is the van der Waals attraction force, P_R the repulsion force of the double layers, P_P the repulsion force of the adsorbed macromolecules, and P_h the hydrostatic force.

The results of the measurement of the equilibrium thicknesses of water films between oil drops stabilised by adsorbed layers of poly(vinyl alcohol) have been published.[21,129,138,139] The thickness of the films h was determined by the light interference method.[88,137] The values of h obtained in relatively concentrated electrolyte solutions (where the thickness of the adsorbed layer is much greater than the effective thickness of the double layer) proved to be much greater than twice the radius of inertia or twice the effective hydrodynamic radius R_h of the spherical macromolecular coils in solution calculated from viscosity measurements. The high thicknesses of the PVA film (up to 80–90 nm) have been explained[138] by the presence in the adsorbed layer of long tails, which produce little change in the hydrodynamic radius of the coil but are strongly manifested as a second surface approaches.

In order to account for the finding that $h > 2R_h$, the author of the present review[129] suggested that the equilibrium thickness of the films is determined not only by the thickness of the adsorbed macromolecules but also by the thickness of the polymolecular hydrate layers bound to them, which can reach several nanometers.[136] It has also been shown[21] that the thickness of the adsorbed PVA layers in emulsion films depends little on the molecular weight of the polymer (for different PVA specimens stabilising emulsions of cyclohexane in water, it amounts to 31–35 nm), but change appreciably when the nature of the non-aqueous phase is altered.

Lyklema and van Vliet[138] measured the hydrostatic force which must be applied to horizontal films stabilised by PVA in order to compensate for the steric repulstion of the adsorbed macromolecules as the surfaces approach one another, subject to the condition that the P_A and P_R contributions are small, i.e. when $P_P = P_h$. The experimental dependences of the equilibrium thickness on the wedging pressure (steric repulsion) (see the dashed curve in Fig.11) show that, with increase in the molecular weight of the polymer, a sharp rise of P_P begins with increasing interparticle distances. The experimental $P_P(d)$ curves for a series of stabiliser specimens are close to the corresponding theoretical relations calculated by the Hesselink–Vrij–Overbeek method on the assumption that (1) the interaction of the adsorbed macromolecules is via long tails and (2) that the distribution of the tails with respect to size is the same in the adsorbed state as in the bulk phase. Hence it was concluded[138] that the long tails extending into the bulk phase play a decisive role in the steric repulsion of adsorbed poly(vinyl alcohol).

Analogous $P_P(d)$ relations have been found also for other PVA specimens stabilising aqueous films in symmetrical emulsions of oil in water.[129,139,140] The sharper increase of P_P observed[129] as the surfaces approach one another compared with the theoretical calculation in terms of the HVO theory was explained by the authors on the grounds that the theory does not take into account the energy consumed in the "expulsion" (at least partial) of water molecules from the gap between the film walls as its thickness decreases, i.e. does not take into account the possible contribution of the structural component of the wedging pressure.

Having expressed the relative change in the film thickness as a function of pressure, Sonntag et al.[139] obtained a linear relation between h/h_0 and P up to $h/h_0 \cong 0.3$. It has also been shown that this relation is relatively insensitive to the molecular weight of the stabiliser (PVA). On further interpenetration of the adsorbed macrmolecules, the repulsion energy rapidly rises. Both in this region and in the linear region, the deformation of the adsorbed layers is reversible and is independent of its duration, i.e. during deformation there is no intertwining of the macromolecules into a coil or their desorption. The linear character of the relation between the pressure and deformation in the initial stage of the interpenetration shows that in the outer regions of the adsorbed layer there are no large segment (unit) concentration gradients, which agrees with Hoeve's model[86] for the distribution of the density of units as a function of distance for macromolecules with a high adsorption energy. In this case there is an appreciable gradient of the density of segments near the interface and a slow decrease in the direction of the bulk solution.

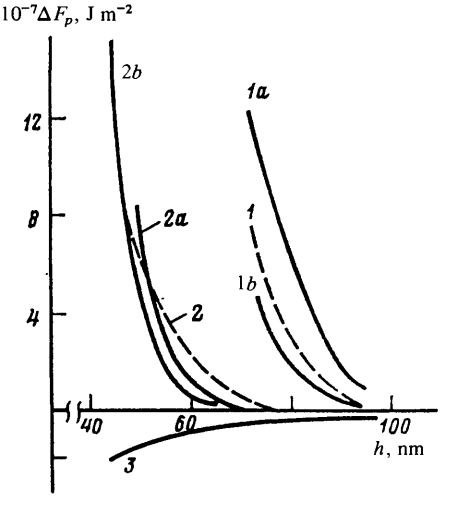

Figure 11. Variation of the steric repulsion of the tails of PVA bound to the oil/water interface and having $M = 1.43 \times 10^5$ (curves *1*) and 4.25×10^4 (curves *2*); dashed curves—experimental data; continuous curves—data calculated by the HVO method for 0.30/1 (curve *1a*), 0.40/2 (curve *1b*), 0.40/1 (curve *2a*), and 0.60/2 (curve *2b*) specimens, where the numerator represents the fraction of units in the form of tails and the denominator the number of tails per polymer molecule; 3) ΔF_A.[138]

It has also been shown[139] that, as the surfaces approach one another, the experimental P_P increases more slowly than would follow from the Hesselink–Vrij–Overbeek theory. This can be attributed to the fact that the real concentration of units in the outer component of the adsorbed HMC layer is higher than is assumed in the theory.

Sonntag et al.[140] measured the steric repulsion of various specimens of poly(vinyl alcohol) adsorbed at the oil/water interface and on quartz filaments as a function of the specific adsorption of the polymer, the molecular weight of the specimen, and the nature and concentration of the added electrolytes. It was concluded that only a small proportion of the tails of the macromolecule (one tail on 30 nm^2 for an average number of units in the tail ($\bar{n} = 500$) or one tail on 20 nm^2 for $\bar{n} = 800$) are responsible for the steric repulsion. With decrease of the number of unhydrolysed acetate groups in the molecule, the thickness of the adsorbed layer also rises, but the steric repulsion diminishes. It has likewise

been observed that, with increase of the KCl concentration in solution from 10^{-3} to 2 M, a sharp rise of P_P begins for increasingly shorter interparticle distances. In conformity with the HVO theory,[114] this shows that the contribution of the osmotic effect to the steric repulsion diminishes with increasing content of the electrolyte in the system. The transition in the lyotropic series from rubidium chloride to lithium chloride leads to the same effect for an unaltered concentration of the added salt.

Cairns et al.[141] developed another approach to the study of the steric repulsion between adsorbed macromolecules; it is based on the idea that this interaction can be characterised as an excess osmotic pressure (Π) in the isotropic disperse system. In other words, the potential energy of the interaction between the particles is expressed in terms of $\Pi = P$. It has been shown that the experimental dependence of Π on the volume fraction Φ_C of poly(methyl methacrylate) particles, stabilised by poly-1,2-stearic acid in dodecane, is close, in the region where $\Phi_C = 0.5-0.6$, to the relation evaluated theoretically from the formula $P = P_A + P_P$, where P_A was calculated by Hamaker's method and P_P was calculated by the statistical Flory–Krigbaum theory [see Eqn.(4)]. For higher values of Φ_C, the experimental Π increase more sharply than the theoretical values, i.e. under these conditions the adsorbed layer is less compressible than predicted by the theory, which assumes a uniform distribution of segments in the adsorbed layer. Hence it is concluded that in fact the concentration of segments in the outer part of the polymer shell is lower than in the inner part.

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Thus direct measurements of the repulsion forces between the adsorbed macromolecules make it possible, firstly, to infer the character of the distribution of the polymer segments in the section of the adsorbed HMC layer, secondly, permit the determination of the mechanism of the stabilisation of polymer-containing dispersions under various conditions, and, thirdly, serve as an instrument for the experimental test of the validity of the theories of the interaction of adsorbed polymer chains.

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Transition Metal Carbonyls Combined with Hydrogen Donors as Initiators of the Radical Reduction of Trichloromethyl Compounds

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The review is devoted to new redox catalysts of the homolytic reduction of trichloromethyl compounds to dichloromethyl compounds—mononuclear and dinuclear metal carbonyls [$Fe(CO)_5$, $Ni(CO)_4$, $M(CO)_6$ (M = Mo, Cr, W), $Mn_2(CO)_{10}$] in combination with hydrogen donors (secondary alcohols, silicon hydrides, mercaptans, tertiary amines, amides, and tetrahydrofuran).
The results obtained hitherto concerning the development of a new radical-chain method for the reduction of a wide variety of trichloromethyl compounds to the dichloromethyl derivatives are surveyed.
The bibliography includes 78 references.

CONTENTS

I.	Introduction	662
II.	Systems based on metal carbonyls and various hydrogen donors	662
III.	Systems based on other transition metal compounds	668
IV.	The mechanism of the reduction reaction. Study by the EPR method	669

I. INTRODUCTION

The ability of $Fe(CO)_5$ to initiate the hydrogenolysis of the C–Cl bond in polychloro-derivatives containing the CCl_3 group under the influence of hydrogen donors with the selective formation of the corresponding dichloromethyl derivatives was discovered by the authors of the present review in 1967;[1,2] since then the reaction based on Scheme (1) has been investigated for a wide range of examples using a wide variety of metal carbonyls (MC) and hydrogen donors (HA).

Scheme 1

$$RCCl_3 + HA \xrightarrow{MC} RCCl_2H.$$

The study of the applications of MC as initiators of radical reactions is a comparatively new field in the chemistry of transition metal carbonyls. The first investigations on these lines date back to 1959–61.[3,4] Many examples of radical addition, telomerisation, polymerisation, cyclisation, disproportionation, and others, initiated by metal carbonyls and their complexes with various ligands, are now known.[5] The evidence for the radical mechanism of the reaction based on Scheme (1), obtained particularly by the EPR method using spin trapping agents (see Section IV), is presented below.

The hydrogenolysis of the C–Cl bond in various polychloro-derivatives has significantly extended the range of applications of various MC and their combinations with nucleophiles for the initiation of radical reactions. We call such systems (MC + nucleophile) coordination initiators based on metal carbonyls; they are also referred to as redox catalysts.[6]

The study of the reduction of trichloromethyl compounds led to the discovery of a number of features of the reactions as a function of the nature of the MC and the hydrogen donor and also as a function of the structure of the trichloromethyl compound.

$Fe(CO)_5$, $Mo(CO)_6$, $Cr(CO)_6$, $W(CO)_6$, $Mn_2(CO)_{10}$, and $Re_2(CO)_{10}$ have been used as initiators, while secondary alcohols, silicon hydrides, mercaptans, tertiary amines, acid amides, and tetrahydrofuran have been employed as hydrogen donors. $Ni(CO)_4$, $HMo(CO)_4P(C_6H_5)_3$, and $MoH_2(\eta\text{-}C_5H_5)_2$ have also been used.

It is noteworthy that, apart from its interest for the chemistry of metal carbonyls, the reduction of trichloromethyl compounds to the corresponding dichloromethyl derivatives is an urgent synthetic problem, since in recent years trichloromethyl compounds have become available as a result of the addition of polyhalogenomethanes (CCl_3X; X = H, Cl, Pr) to olefins and telomerisation,[7,8] while compounds with dichloromethyl groups are less readily available. Methods for the selective reduction $RCCl_3 \rightarrow RCHCl_2$ have undergone little development in previous investigations. The reaction which would be of greatest interest for the solution of the problem formulated, namely the catalytic hydrogenation of $RCCl_3$ compounds, proceeds as "reductive dimerisation" and not as hydrogenolysis of the C–Cl bond:[9,10]

$$2RCCl_3 \xrightarrow[Pd/C]{H_2} RCCl_2CCl_2R.$$

Dichloromethyl compounds are of interest not only for chemical and physicochemical studies but also for practical purposes. We may mention the reduction of DDT and related compounds,[11] the reduction of α-trichloromethyl compounds to the corresponding dichloromethyl derivatives.[12] Trichloro- and dichloro-methyl compounds have found extensive applications as insecticides, herbicides, and plasticisers and in the synthesis of medicinal preparations.

This review is devoted to a survey of data on the applications of transition metal carbonyls in the initiation of the hydrogenolysis of the C–Cl bond and the justification of a fundamentally new method for the conversion of trichloromethyl compounds into the dichloromethyl derivatives.

The only other review on this problem[13] is devoted solely to the synthetic aspect of these reactions.

II. SYSTEMS BASED ON METAL CARBONYLS AND VARIOUS HYDROGEN DONORS

1. Alcohols

(a) The Reduction of CCl_4 and $CHCl_3$

Since carbon tetrachloride is reduced more readily than chloroform, in the presence of reductants with moderate activity it is possible to carry out a selective reduction to chloroform. The $Fe(CO)_5$ + iso-C_3H_7OH system is a reductant of this kind (Table 1, experiment 1). $Mo(CO)_6$ and

$Mn_2(CO)_{10}$ combined with iso-C_3H_7OH enter into a non-selective reaction with partial reduction to CH_2Cl_2 (Table 1, experiments 2 and 3).

Chloroform is reduced with greater difficulty than CCl_4 and $RCCl_3$. Thus the $Fe(CO)_5$ + iso-C_3H_7OH system hardly reduces $CHCl_3$ at 120–140 °C (experiments 4 and 5). $Mo(CO)_6$ and $Mn_2(CO)_{10}$ combined with iso-C_3H_7OH reduce $CHCl_3$ to CH_2Cl_2 in 72–73% yields.

Table 1. The reduction of polychloromethanes CCl_3X by isopropyl alcohol in the presence of metal carbonyls (3 h).[12]

No.	MC	X	[CCl_3X] : [iso-C_3H_7OH] : [MC]	T, °C	F*, %	Yield, %	
						$CHCl_3$	CH_2Cl_2
1	$Fe(CO)_5$	Cl	1:8:0.05	120	100	100	0
2	$Mn_2(CO)_{10}$	Cl	1:8:0.05	120	100	90	10
3	$Mo(CO)_6$	Cl	1:8:0.05	140	100	64	36
4	$Fe(CO)_5$	H	1:8:0.05	120	0	—	0
5	$Fe(CO)_5$	H	1:8:0.05	140	10	—	10
6	$Mn_2(CO)_{10}$	H	1:8:0.1	120	72	—	72
7	$Mo(CO)_6$	H	1:8:0.05	140	73	—	73

*F = degree of conversion of the initial polychloroalkane.

The data in Table 1 clearly demonstrate the sequence of the reactivities of MC: $Mo(CO)_6 \geq Mn_2(CO)_{10} \gg Fe(CO)_5$.

Isopropyl alcohol is not an inert medium for the reaction under consideration. Being a hydrogen atom donor, it is oxidised to acetone and in addition it enters into a series of side processes, which lead to the formation of isopropyl chloride, di-isopropyl ether, propene, and water:[14]

$$RCCl_3 + (CH_3)_2CHOH \xrightarrow{MC} RCCl_2H + (CH_3)_2CO + HCl,$$
$$(CH_3)_2CHOH + HCl \rightarrow (CH_3)_2CHCl + H_2O,$$
$$(CH_3)_2CHCl + (CH_3)_2CHOH \rightarrow [(CH_3)_2CH]_2O + H_2O,$$
$$(CH_3)_2CHOH \rightarrow C_3H_6 + H_2O.$$

The formation of propene leads in a number of instances to the appearance of adducts of the type of $RCCl_2CH_2CHClCH_3$.[14]

(b) The Reduction of ααα-Trichloroalkanes

The reduction of ααα-trichloroalkanes by different MC in isopropyl alcohol has been investigated for molecules with a chain length ranging from two to ten carbon atoms. Table 2 presents the results of the reduction of 1,1,1-trichloropentane. The choice of this compound is associated with the fact that it contains no other functional groups and the length of the hydrocarbon chain is such that it cannot lead to lateral displacements of hydrogen in the radical.[15] On the other hand, the chain is not so short that the C–Cl bond energy depends on it, since the reactivity of CCl_4 and CCl_3CH_3 is significantly higher than that of ααα-trichloroalkanes with longer chains. According to the data in Table 2, it is possible to set up the following activity series of MC in the reaction investigated:

$$Mo(CO)_6 > Mn_2(CO)_{10} > Fe(CO)_5 \gg W(CO)_6 > Cr(CO)_6 \gg Re_2(CO)_{10}.$$

Thus the MC used have been divided into two groups—the active initiators $Mo(CO)_6$, $Mn_2(CO)_{10}$, $Fe(CO)_5$, and the relatively ineffective $W(CO)_6$, $Cr(CO)_6$, and $Re_2(CO)_{10}$. The reactions involving the active MC have a chain mechanism and the yield of 1,1-dichloropentane under the chosen conditions ranged from 5.6 to 9.2 moles per mole of the MC (Table 2). The Table also shows that the best [$C_4H_9CCl_3$] : [iso-C_3H_7OH] ratio for $Fe(CO)_5$ or $Mn_2(CO)_{10}$ is 1 : 8 (experiments 3 and 5). In the presence of $Mo(CO)_6$ a high yield is obtained at an even lower dilution (experiment 1).

Table 2. The reduction of 1,1,1-trichloropentane (3 mmol) by isopropyl alcohol in the presence of metal carbonyls (0.3 mmol) (3 h).[16]

No.	MC	[iso-C_3H_7OH]/[$C_4H_9CCl_3$]	T, °C	F, %	Yield %	Q*
1	$Mo(CO)_6$	3	140	96	90	9.0
2	$Mn_2(CO)_{10}$	3	120	72	65	6.5
3	$Mn_2(CO)_{10}$	8	120	97	84	8.4
4	$Fe(CO)_5$	3	120	63	56	5.6
5	$Fe(CO)_5$	8	120	92	92	9.2
6	$W(CO)_6$	3	140	30	26	2.6
7	$W(CO)_6$	8	140	27	27	2.7
8	$Cr(CO)_6$	3	140	20	11	1.1
9	$Cr(CO)_6$	8	140	44	12	1.2
10**	$Re_2(CO)_{10}$	3	140	0	0	0

*Q = [$RCHCl_2$] : [MC], i.e. the yield of the reduction product in moles per mole of the metal carbonyl ("value").
**0.15 mmol of $Re_2(CO)_{10}$ was employed.

Table 3. The reduction of ααα-trichloroalkanes* $RCCl_3$ by isopropyl alcohol in the presence of metal carbonyls.

No.	MC	R	[$RCCl_3$] : [iso-C_3H_7OH] : [MC]	T, °C	τ**	F, %	Yield, %	Q	Refs.
1	$Fe(CO)_5$	C_5H_{11}	1:9.5:0.14	145	5	100	84	6.0	[18]
2	$Fe(CO)_5$	C_7H_{15}	1:8:0.15	120	3	96	65	4.3	[20]
3	$Mo(CO)_6$	C_7H_{15}	1:8:0.075	140	3	93	72	9.6	[20]
4	$Mn_2(CO)_{10}$	C_7H_{15}	1:8:0.1	120	3	88	79	7.9	[20]
5	$Mn_2(CO)_{10}$	C_8H_{17}	1:8:0.1	120	3	95	68	6.8	[20]
6	$Mo(CO)_6$	$C_{10}H_{21}$	1:8:0.05	140	3	95	74	14.7	[20]

*The reduction of $C_4H_9CCl_3$ (see Table 2); for other examples of the reduction of ααα-trichloroalkanes, see also Refs. 17, 19, and 21.
**τ = reaction time in hours.

Table 3 presents examples of the reduction of ααα-trichloroalkanes with different chain lengths. The data in this Table demonstrate the wide-scale applicability of the proposed method to the reduction of a wide variety of ααα-trichloroalkanes and confirm the high activity of $Mo(CO)_6$, $Mn_2(CO)_{10}$, and $Fe(CO)_5$ in combination with isopropyl alcohol. The amount of MC can be varied within fairly wide limits depending on its nature. The smallest amount of MC has been used in the case of $Mo(CO)_6$ (Table 3, experiments 3 and 6).

(c) The Reduction of Polychloroalkanes

αααω-Tetrachloroalkanes can be obtained by the telomerisation of ethylene with CCl_4; ααaγ-tetrachloroalkanes are obtained by the addition of CCl_4 to α-olefins. The reduction of tetrachloroalkanes containing from 3 to 11 carbon atoms in the molecule by active MC in combination with alcohols has

Table 4. The reduction of αααω-tetrachloroalkanes $CCl_3(CH_2CH_2)_nCl(RCCl_3)$ by alcohols with initiation by metal carbonyls.

No.	*n*	MC	Alcohol	[RCCl3] : [alcohol] : [MC]	*T*, °C	τ	*F*, %	Yield, %	Refs.
1	1	$Fe(CO)_5$	iso-C_3H_7OH	1 : 3—8 : 0.05—0.16	140	3—5	73—100	55—70	[14,17,22, 23]
2	1	$Fe(CO)_5$	cyclo-$C_6H_{11}OH$	1 : 3 : 0.1	140	3.5	83	81	[24]
3	1	$Fe(CO)_5$	$C_6H_5CH_2OH$	1 : 2.6 : 0.11	145	5	100	76	[14]
4	1	$Mo(CO)_6$	iso-C_3H_7OH	1 : 8 : 0.05	140	3	100	98	[23]
5	1	$Mo(CO)_6$	cyclo-$C_6H_{11}OH$	1 : 3 : 0.02	140	3.5	47	45	[24]
6	1	$Mn_2(CO)_{10}$	iso-C_3H_7OH	1 : 8 : 0.05	140	3	78	74	[23]
7	2	$Fe(CO)_5$	iso-C_3H_7OH	1 : 3.3—8 : 0.02—0.15	120—145	3—5	100	67—97	[14,16,22] [25]
8	2	$Mo(CO)_6$	iso-C_3H_7OH	1 : 3 : 0.05	140	3	88	86	[16]
9	2	$Mn_2(CO)_{10}$	iso-C_3H_7OH	1 : 8 : 0.1	120	3	97	85	[16]
10	3	$Fe(CO)_5$	iso-C_3H_7OH	1 : 3.3 : 0.04	145	3	100	42—50	[26]

Table 5. The reduction of αααββ-pentachloro- and αααγ-tetrachloro-alkanes $RCCl_3$ by alcohols in the presence of metal carbonyls.

No.	MC	R	Alcohol	[RCCl3] : [alcohol] : [MC]	*T*, °C	*F*, %	Yield, %	Refs.
1	$Fe(CO)_5$	$CHCl_2$	iso-C_3H_7OH	1 : 8 : 0.1	120	35	14*	[20]
2	$Mo(CO)_6$	$CHCl_2$	iso-C_3H_7OH	1 : 8 : 0.1	140	73	23*	[20]
3	$Mn_2(CO)_{10}$	$CHCl_2$	iso-C_3H_7OH	1 : 8 : 0.1	120	64	40*	[20]
4	$Fe(CO)_5$	$C_6H_{13}CHClCH_2$	iso-C_3H_7OH	1 : 3 : 0.15	130	79	40	[28]
5	$Fe(CO)_5$	$C_6H_{13}CHClCH_2$	cyclo-$C_6H_{11}OH$	1 : 3 : 0.15	130	93	52	[28]

*CCl_2 = CHCl was also obtained in yields of 14% (experiment 1), 42% (experiment 2), and 18% (experiment 3).

been investigated. The results are compiled in Tables 4 and 5. They show that the presence of the chlorine atom in the chain does not have a significant influence on the yields of the corresponding αα*γ*- and ααω-trichloroalkanes compared with the reduction of the unsubstituted ααα-trichloroalkanes. In all cases high yields of the reduced compounds have been obtained under favourable conditions, where the $[CCl_3C_nH_{2n}Cl] : [ROH] : [MC]$ ratios are close to 1 : 8 : 0.1 and the chain reaction proceeds selectively via one chlorine atom of the CCl_3 group.

The formation of the products of the 1,5- and 1,6-shifts of hydrogen in the long-chain radical as side products has been noted in the reduction of ααα-trichloro- and αααγ-tetrachloroalkanes with long chains (with more than 5 carbon atoms) and also of αααω-tetrachloroalkanes starting with $CCl_3(CH_2CH_2)_2Cl$.[19] In the reduction of *gem*-trichloroalkanes with $Fe(CO)_5$ or $Mo(CO)_6$ in combination with isopropyl alcohol such rearrangement proceeds to equal extents, while in the presence of $Mn_2(CO)_{10}$ under the same conditions the rearrangement does not take place.[20]

It is known that the CCl_3 group αααβ-tetrachloroalkanes exhibits a number of characteristic features in chemical reactions. In particular catalytic reduction leads in this instance mainly to dechlorination to 1,1-dichloroalk-1-enes;[9] the reduction of 1,1,2-tetrachloropentane with triethylsilane in the presence of t-butyl peroxide is also accompaned by the formation of $CCl_2 = CHC_3H_7$.[27]

The formation of the dechlorination product has been explained by the fact that the $\dot{C}Cl_2CCl_2H$ radical can be stabilised not only by the abstraction of hydrogen but also by fragmentation with elimination of the chlorine atom in the β-position relative to the radical centre:

$$CCl_3CCl_2H \rightarrow \dot{C}Cl_2CCl_2H \begin{cases} \xrightarrow{HA} CHCl_2CCl_2H, \\ \xrightarrow{-Cl} CCl_2{=}CClH. \end{cases}$$

The fragmentation of radicals with ejection of the β-chlorine atom is a general property of such radicals and has been described in numerous examples of radicals of this type generated by different procedures in various reactions.[29]

As can be seen from Table 5, a dechlorination product, namely trichloroethylene, was obtained in all cases from αααββ-pentachloroethane together with the reduced product. The ratio of the two reaction pathways depends on the nature of the MC. Thus in the presence of $Mn_2(CO)_{10}$ the yields of the reduced product (*sym*-tetrachloroethane) reach 40%, while those of the dechlorinated product (trichloroethylene) are 15–18%. On the other hand, the use of $Mo(CO)_6$ favours the preferential formation of trichloroethylene.

Thus the presence of chlorine in the α-position relative to the CCl_3 group results in the reduction process, which proceeds with a yield of 20–40% and is complicated by the concomitant dechlorination to 1,1-dichloroalk-1-enes.

(d) The Reduction of Trichloromethylcarbinols

The practical importance of the reduction of DDT and trichloromethylcarbinols stimulated the study of its possibility. The results are compiled in Table 6.

ααα-Trichloromethyldimethylmethanol (chlorobutol) and aryl-ααα-trichloromethylmethanols, listed in Table 6, are polyfunctional compounds and are formally capable of a series of side reactions. For example, the reduction of chlorobutol involves also the formation of 1,1-dichloro-2-methylpropene, whose yields depend on the nature of the MC (experiments 1 and 3). Aryltrichloromethylmethanols are secondary alcohols and, by analogy with the reactions of isopropyl alcohol (or cyclohexanol), one may expect the formation of the corresponding ketones.

Table 6 shows, for chlorobutol, that aliphatic α-trichloromethylcarbinols are successfully reduced by isopropyl alcohol in combination with $Fe(CO)_5$, $Mo(CO)_6$, and $Mn_2(CO)_{10}$, the

yields being significantly higher in the presence of the last two MC than in the presence of the first (experiments 1–3).

Aryl-α-trichloromethylmethanols can also be successfully reduced to aryl-α-dichloromethylmethanols by the MC + iso-C_3H_7OH system (Table 6, experiments 4–8). It has been shown that the nature of the substituent in the aromatic ring and the MC employed exert a significant influence on the direction of the process. The reaction proceeds in accordance with the scheme

$$\underset{(I)}{XC_6H_4CH(OH)CCl_3} + \text{iso-}C_3H_7OH \xrightarrow{MC} \underset{(II)}{XC_6H_4CH(OH)CHCl_2} + \underset{(III)}{XC_6H_4CH(CHCl_2)OCH(CH_3)_2};$$

X = H (a), *o*-Cl (b), *n*-CH_3O (c).

The reduction of arylcarbinols (I, a and b) result mainly in the formation of aryl-α-dichloromethylmethanols (II, a and b) (experiments 4 and 5). In the case of the carbinol (Ic) under the same conditions the carbinol (IIc) is hardly formed and the reaction is accompanied by pronounced charring. In order to prevent this, a fiftyfold excess of isopropyl alcohol was employed and $Mo(CO)_6$ or $Mn_2(CO)_{10}$ were used in addition to $Fe(CO)_5$ (experiments 6–8). The product ratio (IIc):(IIIc) then depends on the nature of the MC: in the presence of $Fe(CO)_5$ mainly the ether (IIc) is obtained, while the presence of $Mn_2(CO)_{10}$ the main product is the carbinol (IIc).

Table 6. The reduction of trichloromethylmethanols and DDT by isopropyl alcohol in the presence of metal carbonyls (140 °C, 3 h).

No.	MC	$RCCl_3$	$[RCCl_3]:[iso\text{-}C_3H_7OH]:[MC]$	*T*, °C	Yield, %	Refs.
1	$Fe(CO)_5$	$(CH_3)_2C(OH)CCl_3$	1 : 8 : 0.26	100	38*	[32]
2	$Mo(CO)_6$	$(CH_3)_2C(OH)CCl_3$	1 : 8 : 0.26	80	76	[32]
3	$Mn_2(CO)_{10}$	$(CH_3)_2C(OH)CCl_3$	1 : 8 : 0.13	100	75*	[32]
4	$Fe(CO)_5$	$C_6H_4CH(OH)CCl_3$ (Ia)	1 : 5 : 0.1	70	52	[12]
5	$Fe(CO)_5$	*o*-$ClC_6H_4CH(OH)CCl_3$ (Ib)	1 : (5–50) : (0.1–0.15)	80–100	74–93	[12]
6	$Fe(CO)_5$	*p*-$CH_3OC_6H_4CH(OH)CCl_3$ (Ic)	1 : 50 : 0.15	50	7**	[12]
7	$Mo(CO)_6$	ditto	1 : 50 : 0.15	89	43**	[12]
8	$Mn_2(CO)_{10}$	»	1 : 50 : 0.15	91	72**	[12]
9***	$Fe(CO)_5$	(*p*-$ClC_6H_4)_2CHCCl_3$	1 : 12 : 0.05	100	91	[11]

*$(CH_3)_2C = CCl_2$ is also formed in yields of 17% (experiment 1) or 3% (experiment 3); $Cr(CO)_6$, $W(CO)_6$, and $Re_2(CO)_{10}$ give rise to low yields of reaction products.

**p-$CH_3OC_6H_4CH(CHCl_2)OCH(CH_3)_2$ (IIIc) is also formed in yields of 35% (experiment 6), 34% (experiment 7) or 10% (experiment 8).

***135 °C, 6 h.

Thus the reduction of α-trichloromethylcarbinols by the MC + iso-C_3H_7OH system can be undoubtedly used to synthesise α-dichloromethylcarbinols.

DDT was successfully reduced to DDD by secondary alcohols in the presence of MC with a yield of 70–90%.

Among the *gem*-trichloromethyl compounds with aromatic substituents, trichloromethylbenzene occupies a special place. The presence of the phenyl group in the α-position relative to the CCl_3 group is responsible for the specific features of its chemical behaviour. Thus it has been found that the reduction of $C_6H_5CCl_3$ by $Fe(CO)_5$ is the presence of isopropyl or ethyl alcohol does not lead to the formation of $C_6H_5CHCl_2$. The products are $(C_6H_5CCl_2)_2$ or $C_6H_5CCl = CClC_6H_5$.[11] The synthesis of $C_6H_5CHCl_2$ from $C_6H_5CCl_3$ in a nearly quantitative yield has been described. The reaction proceeds without a catalyst in ethanol in the presence of $P[N(C_2H_5)_2]_3$ [30] or $(C_2H_5)_3N$ and $HPO(OC_2H_5)_2$.[31]

In conclusion of the discussion of the use of alcohols in combination with various MC for the reduction of trichloromethyl compounds, one may note that isopropyl alcohol is most suitable for preparative purposes. In certain cases cyclohexanol is more convenient, since it is possible to use it at atmospheric pressure. Benzyl alcohol is also active in these reactions. It has been shown in relation to the reaction with 1,1,1,3-tetrachloropropane that alcohols such as CH_3OH and C_2H_5OH combined with $Fe(CO)_5$ are in principle capable of reducing the trichloromethyl group to the dichloromethyl group, but 1,1,3-trichloropropane is formed only in a low yield. In the presence of $Fe(CO)_5$, $(CH_3)_3COH$ does not reduce 1,1,1,3-tetrachloropropane.[14]

2. Silicon Hydrides

Reactions are known where, in the presence of catalysts ($AlCl_3$, $ZnCl_2$, etc), silicon hydrides reduce a series of organic compounds—acid chlorides, amides, nitriles, lactones, carbonyl compounds, and monochloroalkanes.[33] This review deals with the results of the use of silicon hydrides in combination with metal carbonyls to reduce the CCl_3 group to $CHCl_2$. Examples of such reactions are presented in Tables 7–9.

Table 7. The reduction of compounds with the trichloromethyl group ($RCCl_3$)* by silicon hydrides ($HSiX_3$) in the presence of iron pentacarbonyl

No.	X	R	$[RCCl_3]:[HSiX_3]:[MC]$	*T*, °C	τ	*F*, %	Yield, %	*Q*	Refs.
1	C_2H_5	Cl	1 : 3 : 0.1	105	5	93	70**		[27]
2	C_2H_5	H	1 : 1 : 0.07	145	5	88	84	12	[27]
3	C_2H_5	CH_3	1 : 1 : 0.1	145	5	98	73	7.3	[34]
4	C_2H_5	C_8H_{17}	1 : 1.1 : 0.06	145	5	—	62	10.3	[35]
5	C_2H_5	$CHClC_3H_7$	1 : 1 : 0.067	145	5	33	13***	—	[27]
6	C_2H_5	$CH_2CHClCH_3$	1 : 1 : 0.1	145	4	80	71	7.1	[17]
7	C_2H_5	$CH_2ClClC_3H_7$	1 : 1.1 : 0.06	145	5	—	55	9.1	[35]
8	C_2H_5	$CH_2CHClC_6H_{13}$	1 : 3 : 0.15	130	3	100	72	5	[28]
9	C_2H_5	$(CH_2CH_2)_2Cl$	1 : 1.1 : 0.1	145	4	99	88	8.8	[17]
10	C_2H_5	$(CH_2CH_2)_2Cl$	1 : 1—1.6 : 0.035—0.13	150	3	98	82—89	23—7	[25,35]
11	C_2H_5	$(CH_2CH_2)_2Cl$	1 : 1.3 : 0.007	145	3	100	92	131	[2]
12	OC_2H_5	$(CH_2CH_2)_2Cl$	1 : 1.3 : 0.007	145	3	47	36****	51	[2]
13	Cl	$(CH_2CH_2)_2Cl$	1 : 1.3 : 0.07	145	3	68	12****	18	[2]
14	*****	$(CH_2CH_2)_2Cl$	1 : 1.3 : 0.11	140	5	73	71	6.5	[26]

*For the reduction of 1,1,1-trichloro-octane, see Table 8.

**CH_2Cl_2 is also formed in 19% yield.

***$CCl_2 = CHC_3H_7$ was also obtained in 15% yield.

****1,1,5-Trichloropent-1-ene was also obtained in yields of 5% (experiment 12) and 56% (experiment 13).

*****CH_3SiCl_2H was used as the hydrogen donor.

In the absence of metal carbonyls, silicon hydrides do not reduce the trichloromethyl group.[2] The reduction of trichloromethyl compounds by the $Fe(CO)_5$ + silicon hydride system has been studied in greatest detail. The data in Table 7 demonstrate the high effectiveness of this system in the reduction of the trichloromethyl group to the dichloromethyl group in polychloromethanes, ααα-trichloroalkanes, αααγ-tetrachloroalkanes, and αααω-tetrachloroalkanes. The reaction has a chain mechanism in all cases—the yield of

reduced compounds varies from 5 to 12.5 moles per mole of $Fe(CO)_5$. The high effectiveness of this system is illustrated by the ease of the reduction of chloroform (Table 7, experiment 2) [the $Fe(CO)_5$ + iso-C_3H_7OH system is ineffective in this reaction (Table 1, experiment 4)] and also by the fact that CCl_4 is reduced with the formation of a mixture of chloroform and methylene chloride (Table 7, experiment 1). The reduction of all the polychloroalkanes containing the CCl_3 group investigated (except ααaβ-tetrachloroalkanes) by $Fe(CO)_5$ and $(C_2H_5)_3SiH$ (Table 7, experiments 3, 4, and 6–11) or CH_3SiCl_2H (experiment 14) proceeds selectively with a high yield of the reduced products:

$$RCCl_3 + HSiX_3 \xrightarrow{Fe(CO)_5} RCCl_2H + ClSiX_3.$$

In the majority of the examples investigated, it was sufficient to use 1–1.3 moles of silicon hydride per mole of the initial polychloroalkane and 5 mole % of $Fe(CO)_5$ (relative to $RCCl_3$) in order to obtain high yields of products. The use of $HSi(OC_2H_5)_3$ and $HSiCl_3$ gives rise to low yields of the reduction products (Table 7, experiments 12 and 13).

Table 8. The reduction of n-$C_7H_{15}CCl_3$ (3 mmol) by $(C_2H_5)_3SiH$ (4 mmol) in the presence of metal carbonyls (0.15 mmol).[36]

No.	MC	T, °C	F, %	Yield, %	Q
1	$Fe(CO)_5$	120	62	60	12
2	$Fe(CO)_5$	140	89	83	16
3	$Mo(CO)_6$	120	53	42*	8.4
4	$Mo(CO)_6$	140	97	67*	13
5	$Mn_2(CO)_{10}$	120	100	100	20

*n-$C_6H_{13}CH = CCl_2$ was also obtained in yields of 10 and 30% at 120° and 140 °C respectively.

Table 9. The reduction of perchloropropene and 1,1,2,3,3-pentachloropropene by silicon hydrides in the presence of $Fe(CO)_5$ (5 mole % for C_3Cl_6 and 7.5 mole % for C_3Cl_5H).[36]

No.	Polychloropropene	$[(C_2H_5)_3SiH]/[C_3Cl_n]$	T, °C	τ	F, %	Yield, %	
						C_3Cl_4H	$C_3Cl_4H_2$
1	C_3Cl_6	1.1	105–110	4	90	52	9
2	C_3Cl_6	1	120	3	91	43	24
3	C_3Cl_6	2	140	6	100	4	50
4	C_3Cl_6	*	140	7	100	5	43
5	C_3Cl_5H	1.7	140	4	85	—	30**

*GKZh-94, a siloxane having the structure $[-Si(C_2H_5)(H)O-]_n$ (32 g), was employed.
**$CCl_2 = CClCH_3$ was obtained in addition in ~1% yield.

The hydrogenolysis of the C–Cl bond by $Fe(CO)_5$, $Mo(CO)_6$, or $Mn_2(CO)_{10}$ in combination with triethylsilane has been investigated for 1,1-trichlorooctane (Table 8).[20] The data in Table 8 show that the most active metal carbonyl is $Mn_2(CO)_{10}$ in combination with triethylsilane. $Mo(CO)_6$ proved to be less effective owing to the occurrence of a dehydrochlorination side reaction. The reactions discussed have a chain mechanism.

It has been shown that, in the reduction of long-chain *gem*-trichloro-alkanes by the MC + $(C_2H_5)_3SiH$ systems a rearrangement with 1,5- and 1,6-migration of hydrogen, noted previously for the reduction of the same compounds by isopropyl alcohol in combination with metal carbonyls, does not occur.[36]

The reduction of trichloromethyl compounds containing a multiple bond proceeds in a more complex manner. It has been shown for 5,5,5-trichloropent-1-ene that the interaction of unsaturated trichloromethyl compounds with various metal carbonyls in combination with isopropyl alcohol or triethylsilane leads to a reduction product in a very low yield at high conversions of the initial polychloroalkene.[36] The reduction of perchloropropene and 1,1,2,3,3-pentachloropropene was more successful;[36] the results are presented in Table 9.

It is noteworthy that the hydrogenation of perchloropropene over PtO_2 (like the hydrogenation of trichloromethylalkanes) leads to a dimeric product—perchlorohexadiene.[37] An analogous result has been obtained also on treatment with CuCl in ethanol.[38]

The reduction of perchloropropene by the $Fe(CO)_5$ + $HSi(C_2H_5)_3$ system takes place non-selectively with formation of a mixture 1,1,2,3,3-pentachloropropene and 1,1,2,3-tetrachloropropene. An increase of temperature and an increase of the $(C_2H_5)_3SiH/C_3Cl_6$ ratio improve the yield of $C_3Cl_4H_2$. Table 9 shows that the reaction can be carried out both with formation of C_3Cl_5H as the main product (experiment 2) and with the preferential formation of $C_3Cl_4H_2$ (experiments 3 and 4). The stepwise course of the process is confirmed by the fact that 1,1,2,3,3-pentachloropropene is capable of being reduced under the same conditions to 1,1,2,3-tetrachloropropene (experiment 5). The attempts to reduce perchloropropene by $Fe(CO)_5$, $Mo(CO)_6$, $Mn_2(CO)_{10}$, and $Mo(N_2)_2 \cdot [(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2$ in isopropyl alcohol were unsuccessful.[36]

3. Mercaptans

Mercaptans are of interest as hydrogen donors becuase of their ready availability, the possible wide variety of their structures, and, in particular, the ease of homolysis of the S–H bond. The interaction of polychloroalkanes with various mercaptants in the presence of $Fe(CO)_5$, $Fe_2(CO)_6(SC_2H_5)_2$, $Mo(CO)_6$, $W(CO)_6$, $Mn_2(CO)_{10}$, and $Re_2(CO)_{10}$ has been investigated in a wide range of examples, namely CCl_4, ααα-trichloroalkanes, ααaω-tetrachloroalkanes, and ααaβω-pentachloropentane.[39–41] The results of the reduction of 1,1,1,7-tetrachloroheptane by n-butanethiol or toluene-α-thiol in the presence of the metal carbonyls enumerated are presented in Table 10. $Re_2(CO)_{10}$ proved to be ineffective in this series too (experiment 8), while the effectiveness of $W(CO)_6$ is low (experiments 4 and 7). A significant difference was discovered between the $Fe(CO)_5$ + R'SH system and the analogous systems with $Mo(CO)_6$ or $Mn_2(CO)_{10}$. In the first instance the reaction has a distinct chain mechanism and the yield of $RCCl_2H$ in moles per mole of the metal carbonyl reaches 16 (experiment 1), while in the other two systems the yield is close to unity. With increase of the molar ratio $[MC]:[Cl(CH_2)_6CCl_3]$ to 0.5, a satisfactory yield of 1,1,7-trichloroheptane is attained (experiments 9 and 10). The increase of the molar ratio $[R'SH]:[RCCl_3]$ from 3:1 to 9:1 (experiments 2 and 5 and also 3 and 6) does not affect the yield of the reduced product. Carbon tetrachloride is smoothly reduced by $Fe(CO)_5$ in combination with butanethiol.[40] The same system does not

reduce chloroform under the same conditions.[40] In all cases the reduction of $RCCl_3$ proceeds selectively to $RCCl_2H$. It has been shown for a series of examples that the process considered obeys the equation

$$RCCl_3 + 2R'SH \xrightarrow{MC} RCCl_2H + R'SSR' + HCl.$$

The following mercaptans have been tested as hydrogen donors: C_4H_9SH,[39-41] $C_6H_5CH_2SH$,[39,41] t-C_4H_9SH[39,41] and C_6H_5SH.[39] The best results were obtained with butanethiol; the use of other mercaptans, in particular of toluene-α-thiol, results in an increase of the yield of side products (cf experiments 1, 9, and 10 with experiments 12–14). The reduction of other αααω-tetrachloroalkanes (containing 3, 5, and 9 carbon atoms in the molecule) and also of 1,1,1-trichloroheptane[41] leads to results similar to those obtained for 1,1,1,7-tetrachloroheptane.

Table 10. The reduction of 1,1,1,7-tetrachloroheptane by mercaptans in the presence of metal carbonyls (140 °C, 3 h).[39,41]

No.	MC	[$Cl(CH_2)_6CCl_3$] : [R'SH] : [MC]	F, %	Yield, %	Q
		n-C_4H_9SH			
1	$Fe(CO)_5$	1 : 3 : 0.05	86	83	16.6
2	$Mn_2(CO)_{10}$	1 : 3 : 0.05	10	10	2.0
3	$Mo(CO)_6$	1 : 3 : 0.05	13	12	2.4
4	$W(CO)_6$	1 : 3 : 0.05	9	7	1.4
5	$Mn_2(CO)_{10}$	1 : 9 : 0.05	13	10	2.0
6	$Mo(CO)_6$	1 : 9 : 0.05	18	11	2.2
7	$W(CO)_6$	1 : 9 : 0.1	7	6	0.6
8	$Re_2(CO)_{10}$	1 : 3 : 0.1	3	1*	—
9	$Mn_2(CO)_{10}$	1 : 3 : 0.5	70	63*	1.2
10	$Mo(CO)_6$	1 : 3 : 0.5	46	42*	0.8
11	$Fe_2(CO)_6(SC_2H_5)_2$	1 : 2.5 : 0.02	—	80	33
		$C_6H_5CH_2SH$			
12	$Fe(CO)_5$	1 : 3 : 0.14	90	69*	4.9
13	$Mn_2(CO)_{10}$	1 : 3 : 0.51	86	68*	1.3
14	$Mo(CO)_6$	1 : 3 : 0.49	60	17*	0.3

*1,1,7-Trichlorohept-1-ene is also formed in yields of 1–3% (experiments 8–10), 16% (experiment 12), 7% (experiment 13), and 26% (experiment 14).

Table 11. The reduction of $CCl_3CHCl(CH_2)_3Cl$ (IV) and $CCl_3CH_2CH(CH_3)CH_2CH_2Cl$ (V) by n-buthanethiol in the presence of metal carbonyls (140 °C, 4 h).[41]

No.	MC	Compound	[$RCCl_3$] : [n-C_4H_9SH] : [MC]	F, %	Yield of $RCHCl_2$, %
1	$Fe(CO)_5$	(IV)	1 : 2.7 : 0.15	100	51*
2	$Fe(CO)_5$	(IV)	1 : 5.6 : 0.18	100	53*
3	$Mn_2(CO)_{10}$	(IV)	1 : 2.7 : 0.48	66	42*
4	$Fe(CO)_5$	(V)	1 : 2.7 : 0.15	100	68**
5	$Mn_2(CO)_{10}$	(V)	1 : 2.8 : 0.50	77	59

*$Cl(CH_2)_3CH = CCl_2$ (VII) was also obtained in yields of 42% (experiment 1), 30% (experiment 2), and 19% (experiment 3) as well as $Cl(CH_2)_3CCl = CCl_2$ (VIII) in yields of 4–5% (experiments 1 and 2).
**$CH_3CHClCH_2CH(CH_3)CH = CCl_2$ (X) was also obtained in 18% yield.

The reactions of 1,1,1,2,5-pentachloropentane (IV) and 1,1,1,5-tetrachloro-3-methylhexane (V) require special consideration (Table 11). As shown above, αααβ-tetrachloro- and αααββ-pentachloro-alkanes undergo two types of reactions with metal carbonyls—reduction and dechlorination. Table 11 shows that, on interaction with both $Fe(CO)_5$ and $Mn_2(CO)_{10}$ in the presence of butanethiol, compound (IV) also gives rise to the reduction product (VI) and the dechlorination product (VII) in comparable yields. The reaction of compound (V), containing in the α-position a methyl side group, with $Fe(CO)_5$ and C_4H_9SH affords, together with the reduction product (IX), also the dehydrochlorination product (X) in a significant yield. Dehydrochlorination does not occur in the presence of $Mn_2(CO)_{10}$.

It is noteworthy that the iron carbonyl complex containing RS ligands, namely $Fe_2(CO)_6(SC_2H_5)_2$, combined with n-butanethiol constitutes a system which is just as effective as the system comprising $Fe(CO)_5$ and n-butanethiol (Table 10, experiments 1 and 11).

4. Tertiary Amines and Amides

Triethylamine, dimethylaniline (DMA), pyridine, and quinoline have been tested as hydrogen donors in the $Fe(CO)_5$ + tertiary amine systems (Table 12). It has been shown for the reaction with 1,1,1-trichloro-octane (Table 12) that dimethylaniline (experiments 1, 2, 6, and 7) and triethylamine (III) are active as hydrogen donors in the reactions investigated, while pyridine (experiment 4) and quinoline (experiment 5) are not, as was to be expected.

Table 12. The reduction of trichloromethyl compounds $RCCl_3$ by tertiary amines in the presence of $Fe(CO)_5$ (130–140 °C).

No.	R	Amine	[$RCCl_3$] : [amine] : [$Fe(CO)_5$]	τ	Yield, %	Refs.
1	CH_3CH_2	DMA	1 : 2.5 : 0.04	18*	68	[35]
2**	$CH_3(CH_2)_6$	DMA	1 : 10.8 : 0.075	18	67	[1]
3**	$CH_3(CH_2)_6$	$(C_2H_5)_3N$	1 : 17 : 0.120	18	69	[1]
4**	$CH_3(CH_2)_6$	pyridine	1 : 11 : 0.075	18	12	[1]
5**	$CH_3(CH_2)_6$	quinoline	1 : 10.9 : 0.076	18	7	[1]
6	$CH_3COO(CH_2)_4$	DMA	1 : 2 : 0.046	5	66	[35]
7	$C_2H_5O(CH_2)_4$	DMA	1 : 2 : 0.073	10	61	[35]

*The reaction was continued until the complete conversion of the initial $RCCl_3$ (gas–liquid chromatographic analysis).
**The experiments were performed in chloroform.

An advantage of this system is the possibility of reducing trichloromethyl compounds containing substituents which are not inert in an acid medium. Thus 5-acetoxy-1,1,1-trichloropentane was reduced by $Fe(CO)_5$ + dimethylaniline with formation of 5-acetoxy-1,1-dichloropentane in 66% yield (experiment 6). 1,1,1-Trichloro-5-ethoxypentane is also reduced smoothyl (experiment 7).

The chemical reactions of dimethylaniline in the process investigated have been elucidated[35] in the reduction of 1,1,1-trichloropropane by the $Fe(CO)_5$ + DMA system. It was found that the main DMA reaction product is the diamine $(CH_3)_2NC_6H_4CH_2C_6H_4N(CH_3)_2$ (XI). The dimer $(CH_3)_2$. .$NC_6H_4CH_2N(CH_3)C_6H_5$ (XII), the trimer $(CH_3)_2NC_6H_4CH_2$. .$N(CH_3)C_6H_4CH_2N(CH_3)C_6H_5$, and methylaniline are also formed in low yields. It has been suggested that compound (XII) is formed initially and is then converted into compound

(XI) and methylaniline according to data of Braun and Kruber:[42]

$$(CH_3)_2NC_6H_4CH_2N(CH_3)C_6H_5 + C_6H_5N(CH_3)_2 \xrightarrow{H^+} (XI) + C_6H_5NHCH_3.$$
(XII)

Indeed it has been shown in a special experiment that heating of compound (XII) with DMA in the presence of diemthylaniline hydrochloride at 140 °C (i.e. under the conditions of the reduction experiments) leads to the formation of compound (XI).[35] On the basis of the foregoing, it is possible to describe the reduction of a *gem*-trichloromethyl compound by DMA + $Fe(CO)_5$ in terms of Scheme 2:

Scheme 2

$$RCCl_3 + 3C_6H_5N(CH_3)_2 \rightarrow RCCl_2H + (CH_3)_2NC_6H_4CH_2N(CH_3)C_6H_5 + \underset{(XII)}{} + C_6H_5N(CH_3)_2 \cdot HCl;$$

$$(XII) + C_6H_5N(CH_3)_2 \rightarrow (CH_3)_2NC_6H_4CH_2C_6H_4N(CH_3)_2 + C_6H_5NH(CH_3).$$
(XI)

Thus it has been demonstrated experimentally that the hydrogen donors in the processes investigated are indeed tertiary amines containing alkyl substituents. Scheme 2 shows that an equimolar amount of the hydrochloride of the amine employed is formed together with the dichloromethyl compound. The formation of the solid amine hydrochloride, which is difficult to separate from the reaction products, complicates their isolation and is an obstacle to the wide-scale employment of tertiary amines as components of the reduction system.

The $Fe(CO)_5$ + DMF system is active in the initiation of radical reactions, but DMF is a comparatively ineffective hydrogen donor. The above system can therefore be used conveniently in the study of the addition, telomerisation, and rearrangement of radicals in reactions involving trichloromethyl compounds where the reduction of the latter becomes a side process.[43]

Table 13. The reduction of polychloroalkanes $RCCl_3$ by DMF in the presence of $Fe(CO)_5$ (135–145 °C, 3–4 h).

No.	R	$[RCCl_3]:[DMF]:[Fe(CO)_5]$	*F*, %	Yield, %	Refs.
1	$Cl(CH_2)_2$	1 : 3 : 0.1	76	24	[17]
2	$Cl(CH_2)_4$	1 : 1 : 0.08	11	7*	[25]
3	$n\text{-}C_6H_{13}CHClCH_2$	1 : 1 : 0.15	72	28**	[28]

*$CHCl_2(CH_2)_3CHCl_2$ is also formed in 1.7% yield.
**The products of the 1,5-H, 1,6-H, 1,7-H, and 1,8-H rearrangements are also formed in an overall yield of 33%.

Certain data obtained in the study of the reactions of $RCCl_3$ with $Fe(CO)_5$ + DMF are presented in Table 13, which shows that, even in reactions with a high degree of conversion of the initial polychloroalkanes (experiments 1 and 3) and for the molar ratio $[RCCl_3]:[DMF] = 1:3$ (experiment 1) the yields of the reduced compound are 24–28% and the yields of the product formed as a result of the rearrangement of hydrogen in the long-chain tetrachloroalkanes is comparable to the yield of the reduced products.

5. Tetrahydrofuran Combined with Nickel Carbonyl

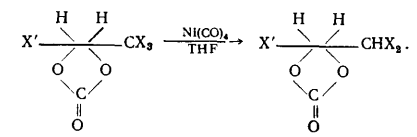
Nickel carbonyl occupies a special place among the metal carbonyls as a component of the reduction system.[44,45] Reduction of the $CHal_3$ group by an excess of $Ni(CO)_4$ under mild conditions in tetrahydrofuran (T) has been investigated (Table 14). The reduction of trichloro- and tribromo-diarylethanes proceeds in accordance with the following scheme:

$$Ar_2CHCX_3 \xrightarrow[THF]{Ni(CO)_4} Ar_2CHCHX_2;$$
(XIII, a and b) (XIV, a and b)
X=Br, Ar=C_6H_5 (a), X=Cl, Ar=*p*-ClC_6H_4 (b)

Table 14. The reduction of the CX_3 group by $Ni(CO)_4$ and THF {40 °C, $[RCX_3]:[THF] = 1:247$}.[45]

No.	RCX_3	X′	$[RCX_3]:[Ni(CO)_4]$	τ	$RCHX_2$	Yield, %
1	(XIIIa)	—	1:2	5	(XIVa)	86
2	(XIIIb)	—	1:2	48	(XIVb)	86
3	(XVa)	H	1:2	24	(XVIa)	38
4	(XVb)	Cl	1:2	48	(XVIb)	53
5	(XVc)	Br	1:2	48	(XVIc)	62
6	(XVd)	CN	1:5	28	(XVId)	48
7	(XVe)	CO_2CH_3	1:3.3	64	(XVIe)	70
8	(XVf)	OCH_3	1:2	48	(XVIf)	59
9	(XVIIa)	Br	1:3	5	(XVIIIa)	69
10	(XVIIb)	CO_2CH_3	1:2.5	2.5	(XVIIIb)	63
11	(XIX)	—	1:2.2	20	(XX)	60

Together with *gem*-trihalogenodiarylethanes, *gem*-trihalogenodioxilans have been reduced by this method. These labile compounds give rise to *gem*-dihalogenodioxolans under the selected conditions (40 °C), which gives rise to the possibility of a transition to aldehydosugars:



X=Cl: (XV,a–e) (XVI,a–e)
X=Br: (XVII, a and b) (XVIII, a and b)

The $Ni(CO)_4$ + THF system makes it possible to reduce selectively the CBr_3 group to $CHBr_2$ (Table 14, experiment 11). Thus 1,1,1,3-tetrabromo-5-phenylpentane (XIX) is reduced to 1,1,3-tribromo-5-phenylpentane (XX) in 60% yield. The reduction of the CBr_3 group, activated by aryl substituents as in compounds (XIIIa), proceeds under mild conditions with a high yield. When other solvents are used (isopropyl alcohol, dioxan, tetrahydrothiophen, cyclohexane, and benzene), there is virtually no reduction. When the reaction was carried out in DMF, the reduction product was obtained in a low yield and the reaction proceeded in a complex manner. An important difference of the reduction reaction in the presence of $Ni(CO)_4$ involves the use of a (2–5)-fold excess of $Ni(CO)_4$ relative to the trihalogenomethyl compound, which hinders the practical application of this method.

III. SYSTEMS BASED ON OTHER TRANSITION METAL COMPOUNDS

Apart from metal carbonyls, metal chlorides,[46] $H_2PtCl_6 \cdot 6H_2O$,[27,46] and $RuCl_2[(C_6H_5)_3P]$[47] can be used in combination with hydrogen donors (silicon hdyrides and secondary

alcohols). The results obtained are presented in Tables 15 and 16. Table 15 shows that copper, cobalt, and chromium chlorides and $H_2PtCl_6.6H_2O$ combined with triethylsilane reduce CCl_4 to $CHCl_3$ in satisfactory yields but not selectively—1–3% of CH_2Cl_2 is also formed despite the presence of an excess of CCl_4. The reduction of both CCl_4 and ααα-trichloroalkanes by $RuCl_2[(C_6H_5)_3P]_3$ in combination with isopropyl alcohol (Table 16) proceeds selectively and with a quantitative yield.

Table 15. The reduction of polychloromethanes ($XCCl_3$) by transition metal complexes and salts (TMS) in combination with hydrogen donors (HA)*.

No.	TMS	HA	X	[$XCCl_3$] : [HA] : [TMS]	T, °C	τ	Yield, %		Refs.
							$CHCl_3$	CH_2Cl_2	
1**	$CuCl_2 \cdot 2H_2O$	$(C_2H_5)_3SiH$	Cl	1 : 0.5 : 0.005	140	5	85	2	[46]
2**	$CoCl_2$	$(C_2H_5)_3SiH$	Cl	1 : 0.5 : 0.005	120	5	49	1	[46]
3**	$CrCl_2 \cdot xH_2O$	$(C_2H_5)_3SiH$	Cl	1 : 0.5 : 0.005	140	10	69	3	[46]
4**	$H_2PtCl_6 \cdot 6H_2O$	$(C_2H_5)_3SiH$	Cl	1 : 0.5 : 0.005	75	10	58	2	[46]
5	$H_2PtCl_6 \cdot 6H_2O$	$(C_2H_5)_3SiH$	Cl	1 : 3 : 0.0075	105	5	65	35	[27]
6	$H_2PtCl_6 \cdot 6H_2O$	$(C_2H_5)_3SiH$	H	1 : 3 : 0.0075	145	5	—	93	[27]
7	$RuCl_2[P(C_6H_5)_3]_3$	iso-C_3H_7OH	Cl	1 : 5 : 0.003	145	2.5	98	—	[47]

*The degree of conversion of the initial polychloromethane was 100%.
**The yield was calculated relative to $(C_2H_5)_3SiH$.

Transition metal hydrides are frequently used for the hydrogenolysis of the C–Cl bond in CCl_4, mainly in order to demonstrate the presence of hydride hydrogen in the molecule. For example, $HMn(CO)_4P(C_6H_5)_3$ [48] and $MoH_2(\eta\text{-}C_5H_5)_2$ have been used as reducing agents.[49] It has been shown that $HMn(CO)_4P(C_6H_5)_3$ reduces CCl_4, taken in a large excess, to $CHCl_3$ at room temperature and the latter is reduced quantitatively to CH_2Cl_2 under the same conditions relative to $HMn(CO)_4P(C_6H_5)_3$. Coordination unsaturated $MoH_2(\eta\text{-}C_5H_5)_2$ reduces CCl_4 stepwise: to $CHCl_3$ at −10 °C and to CH_2Cl_2 at 30 °C. However, reactions of this type are of no preparative value, because they require an equimolar amount of the metal hydride.

Thus is has been established that the transition metal carbonyls $Fe(CO)_5$, $M(CO)_6$ (M = Cr, Mo, or W), and $M_2(CO)_{10}$ (M = Mn or Re) generate the $RCCl_3$ radicals on interaction with trichloromethyl compounds. $Fe(CO)_5$, $Mo(CO)_6$, and $Mn_2(CO)_{10}$ combined with hydrogen donors hydrogenate trichloromethyl compounds to dichloromethyl derivatives. It has been found that $Cr(CO)_6$ and $W(CO)_6$ are ineffective in this reaction. A new radical-chain method has been developed for the reduction of a wide variety of trichloromethyl compounds (ααα-tri, αααβ-tetra-, αααγ-tetra, and αααω-tetra-chloroalkanes, DDT and its analogues, and trichloromethyl compounds containing functional groups).

IV. THE MECHANISM OF THE REDUCTION REACTION. STUDY BY THE EPR METHOD

There exists much chemical evidence for the formation of the $R\dot{C}Cl_2$ radicals in accordance with Scheme 3. Thus it has been found that the chain transfer constants in the telomerisation of CCl_4 with propene initiated by $Cr(CO)_6$ [51] and $Mn_2(CO)_{10}$ [52] agree with the values obtained for the same reaction initiated by peroxides.

The formation of the $\dot{C}Cl_3$ radicals on treatment of CCl_4 with $Mo_2(CO)_6(\eta\text{-}C_5H_5)_3$ has been demonstrated.[53] The reaction of CCl_4 with $Fe(CO)_5$ in the absence of hydrogen donors and unsaturated compounds leads to the formation of CCl_3CCl_3,[54] which can be regarded as proof of the intermediate formation of the $\dot{C}Cl_3$ radical. The presence of the $\dot{C}Cl_3$ and $R\dot{C}Cl_2$ radicals obtained by treating trichloromethyl derivatives with metal carbonyls combined with a nucleophile has been frequently revealed by the addition to olefins and other unsaturated compounds.[5,55]

The radical character of the reduction of the CCl_3 group to $CHCl_2$ under consideration has been unambiguously established by EPR in an investigation of a photochemical interaction of polychloroalkanes containing the CCl_3 group with metal carbonyls and also of the reactions of certain hydrogen donors with metal carbonyls.

1. Reactions of Polychlorohydrocarbons with Metal Carbonyls

Certain data obtained using EPR in conjunction with the spin trapping method are presented in Table 17. In all cases it is possible to identify the nitroxy-radicals $RCCl_2N(\dot{O})R'$—the spin-adducts of the $R\dot{C}Cl_2$ radicals and the R'NO spin trapping agent (experiments 1–4, 6, 8–10, and 13–16), whose formation is described by Eqns (1)–(3) of Scheme 3:

Scheme 3

$$M(CO)_n \rightleftharpoons M(CO)_{n-1} + CO, \quad (1)$$

$$M(CO)_{n-1} + RCCl_3 \rightarrow ClM(CO)_{n-1} + R\dot{C}Cl_2, \quad (2)$$

$$R\dot{C}Cl_2 + R'NO \rightarrow RCCl_2N(\dot{O})R', \quad (3)$$

$$ClM(CO)_{n-1} + R'NO \rightarrow ClM(CO)_{n-1}N(\dot{O})R'. \quad (4)$$

Table 16. The reduction of polychloromethanes $RCCl_3$ by transition metal complexes (TMC) in combination with hydrogen donors (HA).

No.	TMC	HA	R	[$RCCl_3$] : [HA] : [TMC]	T, °C	τ	F, %	Yield, %	Refs.
1	$H_2PtCl_6 \cdot 6H_2O$	Cl_3SiH	$Cl(CH_2)_2$	1 : 1.3 : 0.0001	140	4.5	100	73	[2, 35]
2	$H_2PtCl_6 \cdot 6H_2O$	$(C_2H_5)_3SiH$	$Cl(CH_2)_4$	1 : 1.3 : 0.0001	145	3	100	92	[2]
3*	$H_2PtCl_6 \cdot 6H_2O$	$(C_2H_5)_3SiH$	$CHClC_3H_7$	1 : 1 : 0.0075	145	5	72	40	[27]
4	$RuCl_2[P(C_6H_5)_3]_3$	iso-C_3H_7OH	n-C_4H_9	1 : 9 : 0.002	150	3	98	quant.	[50]
5**	$RuCl_2[P(C_6H_5)_3]_3$	iso-C_3H_7OH	n-C_6H_{13}	1 : 9 : 0.002	150	3	98	quant.	[50]
6**	$RuCl_2[P(C_6H_5)_3]_3$	iso-C_3H_7OH	n-C_8H_{17}	1 : 9 : 0.002	150	3	98	quant.	[50]

*$CCl_2 = CHC_3H_7$ is also formed in 15% yield.
**Benzyl alcohol and cyclohexanol are also effective in this reaction.

Table 17. EPR spectroscopic parameters of the radicals obtained by the photochemical interaction of polychloroalkanes with metal carbonyls in the presence of spin trapping agents.

No.	Initiators	Polychloroalkane	Spin trapping agent	Radical*	a_N, G	a_{Cl}, G	a_H, G	Refs.
1	$Fe(CO)_5$, $Cr(CO)_6$ $Mo(CO)_6$, $W(CO)_6$ $Mn_2(CO)_{10}$	CCl_4	PBN	$CCl_3CH(C_6H_5)N(\dot{O})C(CH_3)_3$ (XXI)	13.4	—	1.3	[56, 57]
2	$Cr(CO)_6$, $W(CO)_6$ $Mn_2(CO)_{10}$	CCl_4	ND	$CCl_3N(\dot{O})Ar$ (XXII)	10.7	1.3	—	[57]
3	$[(C_2H_5)_3Sn]_2$	CCl_4	ND	(XXII)	10.7	1.3	—	[58]
4	$[(CH_3)_3CO]_2$	CCl_4	ND	(XXII)	10.7	1.3	—	[58]
5	$Fe(CO)_5$	CCl_4	MNP	$ClFe(CO)_4N(\dot{O})C(CH_3)_3$ (XXIII)	15.9	0.9	—	[56]
6	$Cr(CO)_6$	CCl_4	ND	(XXII) $ClCr(CO)_5N(\dot{O})Ar$ (XXIV) $Cl\dot{C}r(CO)_4(ArNO)$ $Cl^{53}Cr(CO)_4(ArNO)$ **	10.7 13.7 8.3 8.3	1.3 — — —	— — — —	[58] [59]
7	$Cr(CO)_6$	CCl_4	NB	$ClCr(CO)_5O\dot{N}Ar^1$ (XXV) $Cl\dot{C}r(CO)_4(ONAr^1)$	8.0 6.2	— —	*** —	[59]
8	$Cr(CO)_6$	CCl_4	MNP	$Cl^{53}\dot{C}r(CO_4[(CH_3)_3CNO]$ ** (XXVI) $CCl_3N(\dot{O})C(CH_3)_3$ (XXVII)	7.3 12.5	— 2.2	— —	[59]
9	$Fe(CO)_5$	$HCCl_3$	PBN	$CHCl_2CH(C_6H_5)N(\dot{O})C(CH_3)_3$ (XXI)	14.2	—	2.2	[56]
10	$(Me_3CO)_2$	$HCCl_3$	PBN	(XXI)	13.4	—	1.3	[56]
11	$Fe(CO)_5$	$HCCl_3$	MNP	(XXIII)	16.0	0.9	—	[56]
12	$Fe(CO)_5$	$C_6H_5CH_2Cl$	MNP	(XXIII) $C_6H_5CH_2N(\dot{O})C(CH_3)_3$	15.9 14.2	0.9 —	— 7.2	[61]
13	$Fe(CO)_5$	$ClCH_2CH_2CCl_3$	PBN	$Cl(CH_2)_2CCl_2CH(C_6H_5)N(\dot{O})C(CH_3)_3$	13.8	—	1.7	[62]
14	$(Me_3CO)_2$	$HCCl_2CH_2CCl_2H$	PBN	$HCCl_2CH_2CCl_2CH(C_6H_5)N(\dot{O})C(CH_3)_3$	13.8	—	1.7	[63, 64, 65]
15	$Mn_2(CO)_{10}$	$HCCl_2CCl_3$	MNP	$HCCl_2CCl_2N(\dot{O})C(CH_3)_3$ (XXVIII)	12.8	4.5 and 1.0	—	[57]
16	$(C_6H_5CO_2)_2$	$HCCl_2CCl_2H$	MNP	(XXVIII)	12.8	4.5 and 1.0	—	[57]

*Ar = 2,3,5,6-$(CH_3)_4C_6H$, Ar^1 = 2,4,6-$[(CH_3)_2C]_3C_6H_2$.
**$a_{^{53}Cr}$ = 18.6 G.
***a_H for the *meta*-position.

In a number of instances it has been possible to identify the spin-adducts of the metal carbonyl metal-centred radicals with the spin trapping agent (experiments 5, 6–8, 11, and 12) [Eqns.(2) and (4) of Scheme 3].

The reliability of the assignment of the signals in the spectrum has been confirmed by the literature data and also by the specific synthesis of the test radicals and of their spin adducts by known methods (Table 17, experiments 3, 4, 10, 14, and 16). Thus the radicals obtained on treatment with mononuclear Fe, Cr, Mo, and W carbonyls as well as the dinuclear Mn and Re carbonyls give rise to nitroxy-radicals on reaction with the spin trapping agents α-phenyl-t-butyl-nitrone (PBN),[56,57,60] nitrosodurene (ND),[57,59,60] and 2-methyl-2-nitrosopropane (MNP)[60] (Table 17) (experiments 1, 2, 6, and 8). The parameters of the spectra of these radicals agreed with the literature data.[58,64] In addition it has been shown that the parameters of the spectra of the nitroxy-radicals obtained by the reaction of metal carbonyls with CCl_4 in the presence of ND agree with the parameters of the radicals obtained by a specific synthesis involving the

photochemical interaction of hexaethyldistannane (experiment 3) or t-butyl peroxide (TBP)[58] (experiment 4) with CCl_4 in the presence of ND.

In conformity with the known rules, $\dot{C}Cl_3$ radicals have been obtained by the reaction of $CHCl_3$ with TBP (experiment 10), while the reaction with $Fe(CO)_5$ yielded $\dot{C}HCl_2$ radicals (experiment 9). Their spin adducts with PBN gave rise to different spectra.[56] The treatment of CCl_4 and $CHCl_3$ with $Fe(CO)_5$ in the presence of MNP gave rise to the same spectrum, namely that of the spin-adducts of the iron-containing radical (XXIII) (experiment 5, 11, and 12).

The radicals $ClCH_2CH_2\dot{C}Cl_2$ have been obtained by two procedures: by treating $ClCH_2CH_2CCl_3$ with $Fe(CO)_5$ and by the reaction of benzoyl peroxide with $ClCH_2CH_2CHCl_2$. The EPR spectroscopic parameters of the spin-adducts of these radicals with PBN are identical (experiments 13 and 14).

The reaction of CCl_3CHCl_2 with $MN_2(CO)_{10}$ in the presence of MNP yielded additional information, namely, in conformity with the general rule,[63-65] the two β-chloroatoms in the nitroxy-radical (XXVIII) are non-equivalent (experiment 15). The same nitroxy-radical has been obtained by a specific synthesis—by abstracting hydrogen from $HCCl_2CCl_2H$ by phenyl radicals in the presence of MNP.[63,65] The hyperfine interaction constants (HIC) for the nitroxy-radicals obtained by the two procedures have the same values (experiments 15 and 16).

Much information has been obtained[59] as a result of the study of the radicals formed on treatment of CCl_4 with $Cr(CO)_6$ in the presence of ND (experiment 6), 2,4,6-tris-(t-butyl)nitrosobenzene (NB) (experiment 7), and MNP (experiment 8). Not only the spin adducts of the $\dot{C}Cl_2$ radicals with the spin trapping agent (experiments 6 and 8) but also the spin-adducts of the chromium-containing radicals (XXIV) and (XXV) (experiments 6 and 7) were identified in these experiments. In addition, the chromium-centred radicals $Cl\dot{C}r(CO)_4(ArNO)$ and $Cl^{53}\dot{C}r(CO)_4(ArNO)$ (experiment 6), $ClCr(CO)_4(ONAr')$ (experiment 7), and the radical (XXVI) (experiment 8) were identified. The richness of the information in this instance arises because in the experiments a sufficient concentration of the chromium-centred radicals had been obtained (experiments 6 and 8), it was possible to identify in the EPR spectrum a quartet of triplets due to ^{53}Cr having $I = 3/2$ (the content of this isotope in natural chromium is 9.5%).[66] It is noteworthy that, when $Cr(CO)_6$ is allowed to react with CCl_4, the resulting $Cl\dot{C}r(CO)_5$ radicals add to ND at the nitrogen atom with formation of the spin-adducts (XXIV) (experiment 6) and to NB via the oxygen atom with formation of the radical (XXV) (experiment 7). The signals in the spectrum were assigned to the radical (XXV) taking into account the data quoted by Terabe and Konaka.[67]

2. Photochemical and Thermal Interactions of Metal Carbonyls with Hydrogen Donors

The interactions of mononuclear and dinuclear metal carbonyls with silicon hydrides, isopropyl alcohol, hexamethylphosphoramide (HMP), and DMF have been investigated. Under certain conditions (ultraviolet irradiation), these hydrogen donors do not constitute an inert medium for metal carbonyls. It has been established by EPR that, under ultraviolet irradiation, the reaction of hydrogen donors with metal carbonyls can proceed via at least two pathways. It has been shown for a series of hydrogen donors that the latter are incorporated in the coordination sphere of the metal carbonyl, substituting a CO group. It has been shown[59] that the reaction of $Cr(CO)_6$ with CCl_4 in the presence of MNP and HMP (Table 18, experiment 1) produces, together with the radicals (XXVII) and (XXVI) identified in the absence of HMP (Table 17, experiment 8), also the radicals (XXIX) obtained as a result of the substitution of the CO groups in the metal carbonyl by HMP and MNP molecules. The spin-adducts of the radicals $OP[N(CH_3)_2]_3\dot{M}n(CO)_4$ were identified in the reaction of $Mn_2(CO)_{10}$ with HMP in the presence of MNP and ND (experiment 12).

On the other hand, certain hydrogen donors react with metal carbonyls to form metal carbonyl hydrides.[78] The radicals $(C_2H_5)_3\dot{S}i$ [67,68] $(CH_3)_2\dot{C}OH$, and $OP[(N(CH_3)_2]_2\cdot\dot{N}(CH_3)CH_2$,[69] identified in the form of the spin-adducts with the NB, ND, and MNP spin trapping agents, have been obtained by abstracting hydrogen from $(C_2H_5)_3SiH$ (Table 18, experiments 2, 5, and 6),[67,68] iso-C_3H_7OH (experiments 7–9), and HMP (experiments 10 and 11). The formation of radicals with an unpaired electron on the silicon atom in the reactions of $M(CO)_n$ with $(C_2H_5)_3SiH$ has been confirmed by the hyperfine structure (HFS) of the EPR spectra resulting from the splitting by the nuclei of the ^{29}Si isotope, having a magnetic moment $I = 1/2$ (the content of the ^{29}Si isotope in the natural element is 4.7%).[66]

The reaction of DMF with metal carbonyls results in the formation of complex mixtures of radicals (experiments 13–17), including a radical obtained by the abstraction of hydrogen from the methyl group of DMF and identified in the form of a spin-adduct with MNP (XLI) (experiment 15). In addition spin-adducts of radicals to which the structures $(CH_3)_2\dot{N}$ and $(CH_3)_2N(O^-)\dot{C}H$ have been attributed, were identified (experiment 13). The intermediate formation of metal carbonyl hydrides, which were not identified, has been postulated for the reactions of the metal carbonyls with iso-C_3H_7OH, HMP, and DMF; these hydrides apparently ultimately transfer hydrogen to a molecule of the spin trapping agent.[69] Indeed, the spin-adducts of MNP with hydrogen (XXXIII) (experiments 7, 9, 10, 14, and 17) and the spin-adducts of ND with hydrogen (XXXIV) (experiments 8, 11, and 16) have been identified. The formation of transition metal hydrides on interaction of transition metal complexes with alcohols have been described in some communications.[70,71]

The effectiveness of the transition metal hydride complexes as reductants has been demonstrated in a number of reports [see, for example, the reduction of CCl_4 by $HMn(CO)_4\cdot P(C_6H_5)_3$ or $MoH_2(\eta\text{-}C_5H_5)_2$ (in Section III of the present review)]. The authors present evidence in support of the radical character of these reactions.

On the basis of the data presented above, it is possible to consider the mechanism of the reduction reaction as a whole, when the reacting system contains a trichloromethyl derivative, a metal carbonyl, and a hydrogen donor.

The radical-chain mechanism of the above reactions has been unambiguously established. This means that the mechanism involves, as usual, three stages: chain initiation, propagation, and termination.

In broad outline, without considering the reactions of the hydrogen donor, which will be done below, the initiation consists in the dissociation of the mononuclear metal carbonyl with formation of the coordination-unsaturated species $M(CO)_{n-1}$(B) and CO [reaction (1), Schemes 3 and 4]. The species (B) abstract chlorine from $RCCl_3$ with formation of the radical $\dot{R}CCl_2$ [stage (2), Schemes 3 and 4]. In the presence of dinuclear Mn and Re carbonyls the initial initiation stage involves dissociation in accordance with the scheme

$$(CO)_5M—M(CO)_5 \rightleftarrows 2\dot{M}(CO)_5. \quad (C)$$

The radicals (C) abstract chlorine from $RCCl_3$.

Table 18. EPR spectroscopic parameters of the radicals obtained by the photochemical or thermal interaction of metal carbonyls (MC) with hydrogen donors (HA).

No.	MC	HA	Spin trapping agent*	Radical[2*]	a_N, G	Other HFI constants		Refs.
						X	a_X, G	
1	$Cr(CO)_6$	$OP[N(CH_3)_2]_3+CCl_4$	MNP	(XXVII) (XXVI) $ClCr(CO)_3[ONC(CH_3)_3]$ $\{OP[N(CH_3)_2]_3\}$ (XXIX)	12.5 7.3 7.3	Cl ^{53}Cr P	2.2 18.6 3.3	[59]
2	$Fe(CO)_5$	$(C_2H_5)_3SiH$	NB	$(C_2H_5)_3SiONAr^1$ (XXX) $(C_2H_5)_3{}^{29}SiONAr^1$ (XXXI)	10.3 10.3 —	H-α H-α ^{29}Si	1.9 1.9 5.3	[67,68]
3	$Fe(CO)_5$	$(C_2H_5)_3SiH+CCl_4$	ND	(XXII)	10.7	Cl	1.3	[67]
4	$Cr(CO)_6$	$(C_2H_5)_3SiH+CCl_3CCl_2H$	MNP	(XXVIII)[5*] $ClCr(CO)_4[ONC(CH_3)_3]$[6*] $XCr(CO)_4[ONC(CH_3)_3]$[7*]	12.5 — 7.3 6.3	Cl(1) Cl(2) — —	4.3 1.1 — —	[67]
5	$M(CO)_6$ (M=Cr, Mo, W)	$(C_2H_5)_3SiH$	NB	(XXX)+(XXXI)	10.3 —	H-α ^{29}Si	1.9 5.3	[67]
6	$M_2(CO)_{10}$, (M=Mn, Re)	$(C_2H_5)_3SiH$	NB	(XXX)+(XXXI)	10.3 —	H-α ^{29}Si	1.9 5.3	[67]
7	$Fe(CO)_5$	*изо*-C_3H_7OH	ND MNP	$(CH_3)_2C(OH)N(\dot{O})Ar$ (XXXII) $HN(\dot{O})C(CH_3)_3$ (XXXIII)	14.0 13.3	— H	— 11.8	[69]
8	$Mn_2(CO)_{10}$	*изо*-C_3H_7OH	ND	$Mn(CO)_5N(\dot{O})Ar$ (XXXII) $HN(\dot{O})Ar$ (XXXIV)	16.1 14.0 12.8	Mn — H	8.9 — 12.0	[69]
9	$M(CO)_6$ (M=Cr, Mo, W)	*изо*-C_3H_7OH	MNP ND	(XXXIII) (XXXII)	13.3 14.0	H —	11.8 —	[69]
10	$M(CO)_6$ (M=Cr, Mo, W) $M_2(CO)_{10}$ (M=Mn, Re)	$OP[N(CH_3)_2]_3$	MNP	$OP[N(CH_3)_2]$ $N(CH_3)CH_2N(\dot{O})C(CH_3)_3$ (XXXV) (XXXIII)	14.5 — — 13.3	N H P H	3.1 7.8 0.8 11.8	[69]
11	$M(CO)_6$ (M=Cr, Mo, W) $M_2(CO)_{10}$ (M=Mn, Re)	$OP[N(CH_3)_2]_3$	ND	$OP[N(CH_3)_2]_2$ $N(CH_3)CH_2N(\dot{O})Ar$ (XXXVI) (XXXIV)	13.5 — — 12.8	N H(1) H(2) H	2.0 10.6 8.3 12.0	[69]
12	$Mn_2(CO)_{10}$	$OP[N(CH_3)_2]_3$	MNP ND	$OP[N(CH_3)_2]_3$ $Mn(CO)_4N(\dot{O})C(CH_3)_3$ (XXXVII) $OP[N(CH_3)_2]_3Mn(CO)_4N(\dot{O})Ar$ (XXXVIII)	16.6 17.3 —	Mn Mn P	11.7 12.7 2.1	[69]
13	$M(CO)_6$ (M=Cr, Mo, W)	$HC(O)N(CH_3)_2$	ND	$(CH_3)_2N(O^-)CH(\dot{O})NAr$ (XXXIX) $(CH_3)_2N(\dot{O})NAr$ (XL)	13.7 13.7	H N	7.9 3.7	[69]
14	$Cr(CO)_6$	$HC(O)N(CH_3)_2$	MNP	(XXXIII)	13.3	H	11.8	[69]
15	$Mo(CO)_6$	$HC(O)N(CH_3)_2$	MNP	$HC(O)N(CH_3)CH_2N(\dot{O})C(CH_3)_3$ (XLI)	15.3 — —	N H(1) H(2)	2.4 10.2 9.1	[69]
16	$Mn_2(CO)_{10}$	$HC(O)N(CH_3)_2$	ND	$(CO)_5MnOC(H)N(CH_3)_2$ $N(\dot{O})Ar$ (XLII) (XXXIV)	 13.7 12.8	 H H	 7.9 12.0	[69]
17	$Mn_2(CO)_{10}$	$HC(O)N(CH_3)_2$	MNP	$(CO)_5MnC(H)N(CH_3)_2$ $ON(\dot{O})Ar$ (XLIII) (XXXIII)	 23.3 13.3	 — H	 — 11.8	[69]

*For the significance of the abbreviations used for the spin trapping agents, see text.

[2]*For the designation of Ar and Ar^1, see the footnotes to Table 17.

[3]*g = 1.9983.

[4]*g = 1.9981.

[5]*Concerning the non-equivalence of the two hydrogen atoms in compound (XXVIII) (see Gasanov and Freidlina[65]).

[6]*g = 1.9993.

[7]*g = 1.9982.

Chain termination can proceed, as usual, via many pathways. One of the possible chain termination pathways has been established experimentally. It has been found that some of the $R\dot{C}Cl_2$ radicals recombine during the reduction process with formation of RCl_2CCl_2R, which is dechlorinated to RCCl = CClR whose formation as a side product has been demonstrated in many instances [stage (5) of Scheme 4]. The most complex component of the scheme is the chain propagation stages in which the principal reaction products are generated. These stages apparently depend on the nature of all the components of the reaction and its conditions. At least three types of chain propagation may be noted:

Scheme 4

$$M(CO)_n \rightleftarrows M(CO)_{n-1} + CO, \quad (1)$$

$$M(CO)_{n-1} + RCCl_3 \rightarrow ClM(CO)_{n-1} + R\dot{C}Cl_2, \quad (2)$$

(1), (2): initiation

$$R\dot{C}Cl_2 + HA \rightarrow RCCl_2H + A^{\cdot}, \quad (3)$$

$$A^{\cdot} + ClM(CO)_{n-1} \rightarrow ACl + M(CO)_{n-1}, \quad (4)$$

$$HA + M(CO)_{n-1} \rightarrow HM(CO)_{n-1} + A^{\cdot}, \quad (3a)$$

$$RCCl_3 + A^{\cdot} \rightarrow R\dot{C}Cl_2 + ACl, \quad (3b)$$

$$R\dot{C}Cl_2 + HM(CO)_{n-1} \rightarrow RCCl_2H + M(CO)_{n-1}, \quad (3c)$$

$$ClM(CO)_{n-1} + HA \rightarrow A^{\cdot} + HCl + M(CO)_{n-1}, \quad (4a)$$

(3), (4), (3a), (3b), (3c), (4a): chain propagation (three variants)

$$2R\dot{C}Cl_2 \rightarrow RCl_2CCl_2R \rightarrow RCCl{=}CClR \quad (5)$$

(5): chain termination.

Firstly, the $R\dot{C}Cl_2$ radicals can abstract hydrogen directly from the hydrogen donor [stage (3)]; the reaction chain is propagated by the $M(CO)_{n-1}$ species [stage (4)]. Secondly, the $R\dot{C}Cl_2$ radicals can abstract hydrogen from the metal carbonyl hydride and not from the hydrogen donor [stage (3c)]; the chain is again propagated by the same $M(CO)_{n-1}$ species. Stage (4a) differs from stages (3), (4), and (3a)–(3c) by the fact that $ClM(CO)_{n-1}$ reacts with the hydrogen donor to form the chain-propagating $M(CO)_{n-1}$ species.

Chemical investigations have established that a hydrogen atom is split off from the hydrogen donor during the reaction with formation of the hydrogen donor oxidation products: acetone, chlorotriethylsilane, the disulphide RSSR, and di- and tri-amides from isopropyl alcohol, silicon hydrides, mercaptans, and dimethylaniline respectively. It has been demonstrated unambiguously by EPR that this splitting off process has a radical mechanism, since the $(CH_3)_2\dot{C}OH$,[69] $(C_2H_5)_3\dot{S}i$,[67,68] $OP[N(CH_3)_2]N(CH_3)\dot{C}H_2$,[69] and $HC(O)N.(CH_3)\dot{C}H_2$ [69] radicals, derived from isopropyl alcohol, triethylsilane, HMP, and DMF respectively, have been identified.

Taking into account the entire information contained in the EPR spectra obtained, the reaction schemes incorporating stages involving reactions of the hydrogen donors are considered below. Schemes 5 and 6, proposed by Gasanov,[69] are presented below in relation to the reactions of $Mn_2(CO)_{10}$ with HMP and the reactions of metal carbonyls with DMF:

Scheme 5

$$Mn_2(CO)_{10} \rightleftarrows 2\dot{M}n(CO)_5,$$

$$\dot{M}n(CO)_5 + OP[N(CH_3)_2]_3 \rightarrow HMn(CO)_5 + OP[N(CH_3)_2]_2N(CH_3)\dot{C}H_2, \quad (XLIV)$$

$$(XLIV) + RNO \rightarrow OP[N(CH_3)_2]_2N(CH_3)CH_2N(\dot{O})R, \quad (XXXV), (XXXVI)$$

$$HMn(CO)_5 \rightarrow HC(O)Mn(CO)_4,$$

$$HC(O)Mn(CO)_4 + OP[N(CH_3)_2]_3 \rightarrow HC(O)Mn(CO)_4\{OP[N(CH_3)_2]_3\},$$

$$HC(O)Mn(CO)_4\{OP[N(CH_3)_2]_3\} \rightarrow H\dot{C}O + OP[N(CH_3)_2]_3\dot{M}n(CO)_4,$$

$$H\dot{C}O + RNO \rightarrow HN(\dot{O})R, \quad (XXXIII), (XXXIV)$$

$$OP[N(CH_3)_2]_3\dot{M}n(CO)_4 + RNO \rightarrow OP[N(CH_3)_2]_3Mn(CO)_4N(\dot{O})R; \quad (XXXVII), (XXXVIII)$$

R=C(CH$_3$)$_3$; 2, 3, 5, 6-(CH$_3$)$_4$C$_6$H.

The radicals (XLIV) have been obtained by an independent procedure involving the treatment of HMP with TBP and have been identified by EPR using the same trapping agents[78] as in Scheme 3. The radicals (XXXIII)–(XXXVIII) have been identified by EPR.

Scheme 6

$$M(CO)_n + HC(O)N(CH_3)_2 \rightarrow [M(CO)_n]^{\ddagger} + H\dot{C}(O^-)N(CH_3)_2,$$

$$(XLV) \rightarrow H\dot{C}O + \bar{N}(CH_3)_2, \quad (XLV)$$

$$\bar{N}(CH_3)_2 + [M(CO)_n]^{\ddagger} \rightarrow \dot{N}(CH_3)_2 + M(CO)_n, \quad (XLVI)$$

$$H\dot{C}O + HC(O)N(CH_3)_2 \rightarrow H_2 + HC(O)N(CH_3)\dot{C}H_2 + CO, \quad (XLVII)$$

$$(XLVI) + HC(O)N(CH_3)_2 \rightarrow HN(CH_3)_2 + (XLVII).$$

In addition, the reaction of DMF with $Mn_2(CO)_{10}$ involves the formation of adducts by $Mn(CO)_5$ via the carbonyl group, namely $(CO)_5MnCH(\dot{O})NMe_2$ (XLVIII) and $(CO)_5MnO\dot{C}HN.(CH_3)_2$ (XVIX).

The radicals (XLV)–(XLIX) have been detected by EPR using MNP and MD as the spin trapping agents (Table 18, experiments 13–17).

It is noteworthy that the hypothesis that the formyl radicals $H\dot{C}O$, unidentified by Gasanov,[69] are formed in Schemes 5 and 6 has analogies in the literature. Thus it has been assumed[71,72] that the exchange of a carbonyl group in $HMn(CO)_5$ for ^{13}CO proceeds via the 1,2-migration of the CO group with its subsequent ejection from the rearranged molecule:

$$HMn(CO)_5 \xrightarrow{1,2\text{-}CO} HC(O)Mn(CO)_4 \xrightarrow{+{}^{13}CO} HC(O)Mn(CO)_4({}^{13}CO) \xrightarrow{-CO} HMn(CO)_4({}^{13}CO).$$

This is analogous to the formation of $HC(O)Mn(CO)_4$ in one of the stages of Scheme 3.

It has been postulated[73] that vinyl polymerisation initiated by $HMn(CO)_5$ can also involve the formation of $H\dot{C}O$ radicals as a result of the 1,2-migration of the CO group with subsequent elimination of the formyl radical.

The data obtained show that the interaction of metal carbonyls with hydrogen donors has a radical character. Its mechanism is extremely complex and depends both on the nature of the metal carbonyl and on the structure of the hydrogen donor. It is natural to suppose that, apart from the reactions indicated in Schemes 5 and 6, the radicals formed as intermediates in the trichloromethyl derivative + metal carbonyl + hydrogen donor system can also enter into other reactions. It has been shown that metal carbonyls in the systems investigated interact not only with the trichloromethyl derivatives but also with the hydrogen donors and thus participate both in the chain initiation stage and in the chain propagation stages. Whereas all the Fe, Cr, Mo, and W monocarbonyls and the dinuclear Mn and Re carbonyls investigated are capable of abstracting Cl from the CCl_3 group, i.e. of participating in the initiation stage, the successful reduction of CCl_3 to the $CHCl_2$ group can be achieved only with the aid of $Fe(CO)_5$, $Mo(CO)_6$, and $Mn_2(CO)_{10}$. Evidently this can be accounted for by the difficulties in other stages of the process. In particular there is a significant difference between the carbonylation capacities of the Mn and Re compounds; carbonylation by the Mn compounds proceeds much more readily[74–77] [cf Stage (4) in Scheme 3].

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Thus a fundamentally new radical-chain method for the reduction of trichloromethyl compounds to dichloromethyl derivatives by iron, molybdenum and manganese carbonyls

combined with hydrogen donors has been examined in the present review. The stages involved in a series of radical reactions in the $RCCl_3$ + MC + HA systems have been confirmed experimentally by EPR in conjunction with a spin trapping technique and also by chemical studies. It has been shown that iron, molybdenum, and manganese carbonyls participate not only in the initiation stage (with formation of $R\dot{C}Cl_2$) but also in the subsequent stages involving the formation of dichloromethyl compounds on interaction with trichloromethyl compounds in the presence of hydrogen donors. It has been found that the metal carbonyls interact not only with the trichloromethyl compounds but also with the hydrogen donors (alcohols, silicon hydrides, and DMF) via a radical mechanism.

The process schemes examined are important not only for the understanding and regulation of the reactions involving the reduction of CCl_3 to $CHCl_2$ but also for more complex systems. In particular, chain radical addition and telomerisation reactions in trichloromethyl compound + metal carbonyl + nucleophilic coinitiator + unsaturated compound systems must include a series of stages similar to those characterised in the present review.

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Metal-containing Complexes of Lactams, Imidazoles, and Benzimidazoles and Their Biological Activity

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The results of the latest investigations of the problem of the synthesis of metal-containing complexes of lactams, imidazoles, and benzimidazoles, their structure, and their stability in solutions are surveyed. Some data on their biological activity (pesticide and pharmacological) and the mechanism of their physiological action are presented.
The bibliography includes 190 references.

CONTENTS

I. Introduction 676
II. Complexes of lactams 676
III. Metal complexes of imidazoles and benzimidazoles 680
IV. Biological activity of complexes of lactams, imidazoles, and benzimidazoles 684

I. INTRODUCTION

One of the aspects of the use of coordination compounds of transition metals is their application as biologically active substances. The involvement of metal ions and their complexes in biological processes has been described in a number of monographs.[1-4] Recently the attention of investigators has been attracted increasingly by biocoordination compounds which can be used as biologically active preparations in medicine and agriculture.[5-11] The employment of complexes of microelements with biologically active substances such as vitamins, hormones, nucleic acids, etc. is of interest in medical practice. Many medicinal drugs behave as ligands which interact specifically with the ions of a particular metal or group of metals. A series of preparations with anticancer, antibacterial, and antiviral activities have been obtained in recent years on the basis of metal complexes; some of these are used in clinical and experimental medicine.

In view of their toxicity and high phytocidal activity inorganic salts of microelements have not found extensive application in agriculture. However, complexes containing microelements and organic compounds are as a rule more active biologically and less toxic. In the assortment of chemical plant protecting agents available throughout the world, metal-containing compounds occupy an important place.[12] Thus, one of the groups of fungicides consists of various copper compounds which are widely employed in the fight against plant diseases; in some of these diseases, the copper compounds cannot be replaced by other preparations.

The complexes proposed for use in agriculture are as a rule more effective even at lower concentrations than metal ions and organic molecules which enter into their composition. They provide the microelements lacking by the plants, are not phytotoxic, have a broad spectrum of activity, are resistant to the action of light and heat, and, what is most important, are not toxic to warm blooded animals or their toxicity is low. The complexes make it possible to combine in one molecule several biometals or several different molecules with biological activity and acting synergistically, which results in an appreciable enhancement of the overall effect. The complexes act more slowly than salts, but their activity is more prolonged and involves no risk for agricultural crops.

Preparations based on complexes greatly improve the pesticidal qualities of polymeric materials and compositions based on them. The use of complexes and salts mixed with other pesticides to prepare biocidal paints for the coating of the bottoms of ships and other underwater constructions is effective.[13]

The rapid development of biocoordination chemistry is directly related also to the study of the role of metal complexes in processes important in living organisms. One of such problems involves the study of the mechanism of the action of physiologically active substances on biological membranes, enzymes, etc. Here membrane-active compounds, promoting the selective transfer of metal ions through biological and artificial membranes, which is basically related to the complex formation process, are of considerable importance.

Among the various classes of biologically active coordination compounds, complexes with nitrogen-containing heterocycles as ligands have attracted attention.[14] The metal-containing complexes of lactams and azoles, which play an important role in biological processes and have also found applications in pharmocological preparations and as effective plant protecting agents, are promising in this sense.

The present review is devoted to the latest advances in the field of complexes of transition metal salts with certain nitrogen-containing heterocyles—lactams, imidazoles, and benzimidazoles. It describes the current data on the synthesis, structure, and biological activity of these complexes.

II. COMPLEXES OF LACTAMS

The complexes of lactams with heavy metal salts (I) were first obtained in the 1950's.[15]

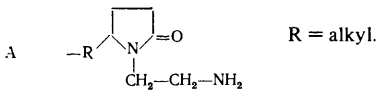
$$MX_m \cdot nA \quad \text{(I)}$$

M = Fe, Co, Ni, Cu;
X = halogen;
$m = 2$;
$n = 3.8$;
A = amide, lactam.

Compounds (I) are readily formed from the initial reactants on heating to 40–160 °C in the presence of a solvent [tetrahydrofuran (THF), methanol, and ethanol] or in the presence of an excess of the initial amide.[15-17] As a rule, between 3 and 10 moles of the amide are used per mole of the metal salt.

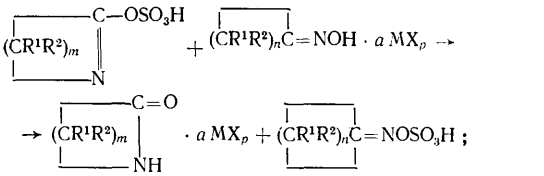
Madan and co-workers[18-20] proposed a method of synthesis of copper-containing complexes of lactams by the interaction of the latter with copper(I) chloride subjected to preliminary dehydration by boiling in 2,2-dimethoxypropane for 2 h. A series of metal complexes of butyrolactam and ε-caprolactam were synthesised in this way. The complexes of 8-caprolactam with cobalt salts have been described.[21] They are obtained in solution in orthoformic ester (tri-isopropoxymethane).

The complexes of 5-alkyl-1-(β-aminoethyl)-2-pyrrolidinones with platinum and palladium salts[22] having the formula (I) with M = Pt or Pd, X = Cl or Br, and $m = n = 2$ have also been synthesised:



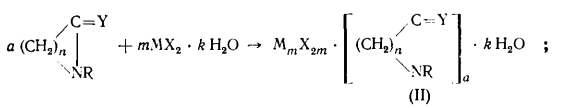
R = alkyl.

Another method of synthesis of metal complexes of lactams[23,24] consists in the reaction between lactam *O*-sulphates and complexes of alicyclic ketoximes with metal halides (Lewis acids):



$m, n = 3—11$, R^1, $R^2 = H$, alkyl, alkenyl;
M = Cu (II), Zn, Al, Sn (II), Sb (III), B, Zr (IV), Fe (III), Ni (II).

The complexes of unsubstituted and *N*-substituted lactams and thiolactams with heavy metal salts having the general formula (II) have been described.[35-38] They are obtained by the reaction of the corresponding lactams with heavy metal salts in absolute ethanol at room temperature or on boiling:



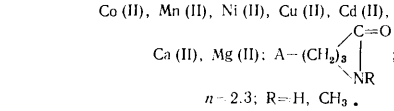
(II)

$a = 1—4$; $n = 3,5$; $m = 1,2$; $k = 0—2$;
M = Cu (II), Zn, Mn (II), Hg (II), Ni (II), Y = O, S;
X = Cl, Br, NO_3; R = H, Ph, CH_3, —CHCCl₃ (OH).

Complexes of a similar type, where the complex-formation reaction proceeds without the elimination of a mobile hydrogen atom, are usually crystalline compounds which contain water of crystallisation derived from the solvent or from the surrounding medium. They can be converted into anhydrous complexes by recrystallisation from an anhydrous solvent such as THF. The complexes (I) are as a rule soluble in water and many organic solvents. The solutions produced are usually stable, but sometimes the complex decomposes on heating into the initial amides and heavy metal salts. Heating of the complexes above the melting point can also lead to decomposition into the initial components. Compounds (I) can be employed as catalysts of the carbonylation reaction and in many instances their catalytic activity is higher than that of the simple salts.[15] The complexes described[18-20] are stable under normal conditions and do not undergo photochemical decomposition and decomposition on heating to 120 °C. All the caprolactam complexes investigated behave as powerful electrolytes.

Recently numerous studies devoted to the determination of the structure and stability of the lactam complexes have appeared in the literature.[39-44] As a rule, infrared and ultraviolet spectroscopy, NMR, EPR, X-ray diffraction, and X-ray spectroscopy are used for the determination of the structures. The infrared spectroscopic and NMR methods make it possible to determine reliably the type of coordination in the complexes of lactams. Coordination to the complex-forming agent takes place as a rule via the oxygen atom, which is demonstrated by the bathochromic shift of the carbonyl group frequency by 30—40 cm^{-1} compared with the free lactam. The small changes in the NH stretching vibration frequencies in the infrared spectra indicate merely a general rearrangement of the ligand molecule in the course of the complex formation process. Lactams behave as monodentate ligands. The stability constants of the complexes are determined as a rule polarographically and by potentiometric titration. Certain physicochemical properties of the metal complexes of lactams have been investigated.[42-44] The number of molecules of water of crystallisation has been determined by the derivatographic method and the molar conductance of the melts and solutions of these complexes has been investigated.

The physicochemical properties of the lactam complexes have been studied in greatest detail by Madan and co-workers.[18-20] It has been shown that the coordination of the ligand to the transition metal is via the carbonyl oxygen atom of the ligand. The perchlorates of these complexes have the general formula



$n = 2.3$; R = H, CH_3.

However, the halogen-containing complexes of Co^{2+}, Cu^{2+}, Mn^{2+}, and Fe^{3+} exhibit appreciable structural differences in relation to the perchlorate complexes. An octahedral structure of the cation and a tetrahedral structure of the anion are characteristic of the cobalt complexes $[CoA_6]^{2+}[CoX_4]^{2-}$, where X = Cl, Br, I, or NCS. The copper and manganese complexes incorporate one or two molecules of the ligand A: MA_2Cl_2 and $MACl_2$. The iron chloride complex has the formula $[FeA_4Cl_2][FeCl_4]$. All these complexes have been characterised by the infrared and electronic spectra and their electrical conductivities and magnetic susceptibilities have been studied.

The coordination compounds of zinc complexes of lactams have been investigated.[45] The compounds obtained were identified by infrared spectroscopy and some of their properties were studied: molar conductance and thermal stability, which is important in connection with the use of such compounds as lactam polymerisation activators. It has been shown that the bond between the zinc atom and the lactam is formed via the oxygen atom. All these complexes contain neither water nor a solvent. The enlargement of the lactam ring on passing from caprolactam to caprylolactam in the case of chloride and bromide complexes does not affect the molecular structure. In the iodide- and thiocyanate-containing complexes the enlargement of the lactam ring entails the coordination of a smaller number of molecules. The complex cation $[ZnA_6]^{2+}$ is not formed in the presence of these anions. The greatest thermal stability is shown by bromides and then by the chlorides.

Complexes of tervalent chromium salts with pyrrolidinone and caprolactam have been described.[48] Their structure has been demonstrated with the aid of infrared spectra. The composition and structure of complexes of 5-alkyl-1-(β-aminoethyl)-2-pyrrolidinones with platinum and palladium salts have been established.[22] Comparison of the infrared spectra of the complexes and the initial ligands reveals an appreciable bathochromic shift of the $\nu(NH_2)$ bands, which indicates the involvement of the amino-nitrogen atom in coordination to the metal. The presence in the spectra of the initial ligands of a broad band associated with the stretching vibrations of the NH_2 group at 3400—3300 cm^{-1} and the fairly low stretching vibration frequency of the carbonyl group (1705—1709 cm^{-1}) indicate the presence of an intramolecular hydrogen bond in the ligands. Complex formation involves the rupture of the

hydrogen bond, which is demonstrated by the increase of $\nu(C{=}O)$ to 1722 cm^{-1}. The latter finding is also confirmed by the fact that the C=O group of the ligand does not participate in coordination (otherwise its frequency in the spectrum of the complex would have been lower than that of the free ligand). The nitrogen atom of the heterocycle is also not involved in complex formation, which can be accounted for by the presence of the mesomeric effect, which reduces the electron density at the ring nitrogen atom.

Thus analysis of the physicochemical data of various workers (mainly infrared spectroscopic data) permits the conclusion that in the complexes of unsubstituted and *N*-alkyl-substituted lactams the ligand is coordinated to the metal via the oxygen atom, while in the complexes of 1-(β-aminoethyl)-substituted lactams coordination is via the amino-nitrogen. The nitrogen atom of the heterocycle is not involved in complex formation.

The structure of compound (II), described in a number of patents,[35-38] has been demonstrated with the aid of infrared spectra; the presence of molecules of water of crystallisation has been confirmed by the derivatographic method and the molar conductances of the complexes have also been investigated.

Compounds (II), namely dipyrrolidinocopper(II) dichloride and tricaprolactamocopper(II) dichloride monohydrate, have been investigated by X-ray diffraction and X-ray spectroscopy.[51-52] The structure of the single crystal of $Cu(P)_2Cl_2$, where P = pyrrolidinone, has been described and is illustrated in Fig. 1. The molecules in the crystal are combined into dimers with highly asymmetric Cu...Cl...Cu bridges. The

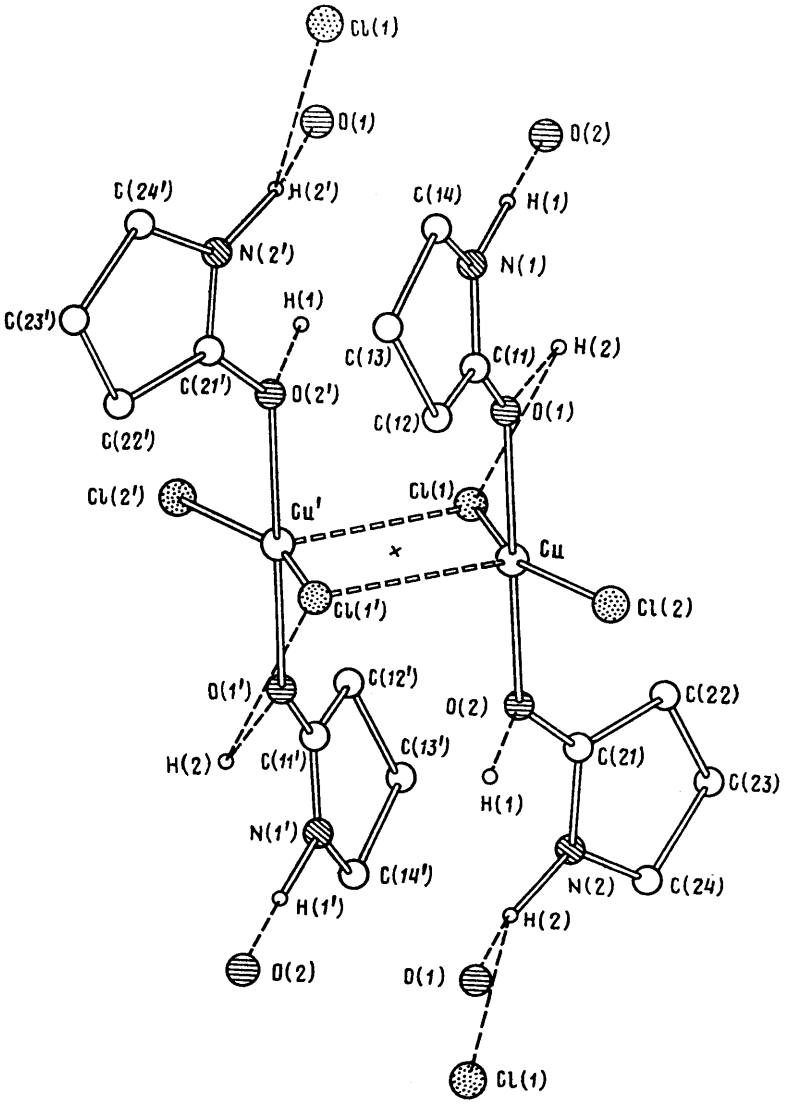


Figure 1. The structure of the dimer in the crystal structure of the $CuCl_2$ complex of 2-pyrrolidinone; the H atoms of the CH_2 groups are not shown.[51]

coordination of the copper atom is intermediate between square and trigonal-bipyramidal (with the ligand atoms in the axial positions). The free coordination site in the *trans*-position relative to the chlorine atom is not completely shielded (<159°).

A different picture obtains for the complex with caprolactam. The structure of tricaprolactamocopper(II) dichloride monohydrate is ionic (Fig.2). The complex is made up of the $[Cu(CL)_6]^{2+}$ cations (CL = caprolactam), which possess crystallographic symmetry with the Cu^{2+} ion at the centre of symmetry, and the anions $[CuCl_3(CL)]^-$, whose number is twice as great. Thus the complex has the formula $[Cu(CL)_6]^{2+}[CuCl_3(CL)]_2^-$. The molecule of water of crystallisation is evidently split off at the instant of the growing of the single crystal. Like pyrrolidinone, caprolactam is a monodentate ligand and is coordinated to the copper atom via the oxygen atom.

The copper atom in the anion has a coordination number of 4 (three Cu–Cl bonds and one Cu...O bond). On the other hand, in the cation copper has a coordination of 4 + 2, i.e. four normal coordinate bonds and two weakened Cu–O(4) and Cu–O(4′) bonds. They correspond to extremely weak metal–oxygen interactions. The caprolactam has in all cases the chair configuration, which is also characteristic of free caprolactam. The cations and anions are combined via hydrogen bonds into an infinite puckered layer.

Analysis of the infrared spectra of compounds (II) has shown that the vibration frequencies of the carbonyl group are reduced by 40–45 cm^{-1} compared with the free ligands. The involvement of the oxygen atom in complex formation cannot fail to alter the lactam system and displacements are therefore observed in the region of the ν(NH) stretching vibration frequencies, but the M – N bond is not formed. It follows from the foregoing that the lactam complexes have

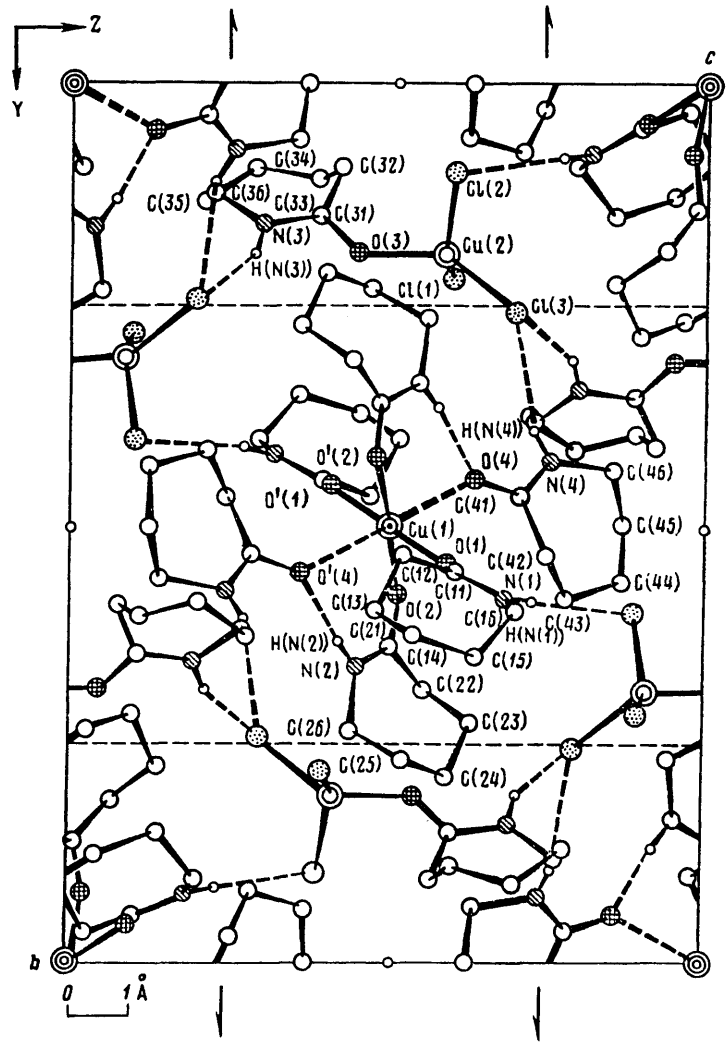


Figure 2. The structure of the $CuCl_2$ complex of caprolactam projected along the a axis (the H atoms of the CH_2 groups are not shown); the dashed lines represent the hydrogen bonds and the additional coordination interactions.[52]

completely different structures depending on the size of the lactam ring. The pyrrolidinone complex has a covalent structure and is dimeric in the crystalline state, while the caprolactam complex has an ionic structure and consists of a polymer.

Analysis of the literature quoted in this Section shows that all the lactam complexes with heavy metal salts are readily soluble in water and polar organic solvents and sparingly soluble in non-polar solvents; they are stable under normal conditions and behave like strong electrolytes.[18-20]

The complexes may or may not contain molecules of water of crystallisation. The most convenient methods of their synthesis are based on the direct interaction of the ligand with heavy metal salts in a polar solvent.

Modern physicochemical methods are used to establish their structures: infrared and ultraviolet spectroscopy, NMR, EPR, and determinations of electronic conductivity and magnetic susceptibility. However, the most reliable methods, which unambiguously establish the structure of the complex and the spatial disposition of the atoms in the molecule, are X-ray diffraction and X-ray spectroscopy.

Unfortunately these methods cannot be used to determine the structures of all complexes, as X-ray diffraction involves the growing of a single crystal and this cannot be achieved in all cases.

III. METAL COMPLEXES OF IMIDAZOLES AND BENZIMIDAZOLES

The early studies on the chemistry of coordination compounds of imidazoles and benzimidazoles were described in the review of Garnovskii et al.[61] A paper on the synthesis and structure of complexes of azoles with metal halides was published later.[62]

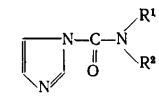
The complexes of azoles are usually obtained by the interaction of the components on heating in organic solvents or by fusing azoles together with metal halides.[63-72] These methods of synthesis frequently lead to compounds containing a large number of solvent molecules. In order to obtain complexes with low coordination numbers, the decomposition of their solvates *in vacuo* at 80–150 °C is therefore employed. In certain cases the presence of solvents leads to the formation of solvolysis and substitution products.

In the case of sparingly soluble metal salts, the ligand exchange method is used. For this purpose, one obtains initially relatively unstable and readily soluble complexes of the salts MX_n (X = halogen), for example, with ethers or acetonitrile, and they are then used in reactions with solutions in imidazole or benzimidazoles. In particular, such a method has been used to synthesise copper(I) complexes. The ligand exchange reaction is carried out in an inert atmosphere.[73-76]

The complexes synthesised can contain between one and six ligand molecules. The number of coordinated groups depends little on the basicity of the imidazole derivatives, but basicity is important in the synthesis of compounds with benzimidazole and its usbstituted derivatives. Thus, imidazole (pK_a = 7) complexes containing from one to six azole molecules have been isolated,[65-70] while only compounds having the composition $MX_2.4HA$ are readily obtained from benzimidazole (pK_a = 5.53).[74,75]

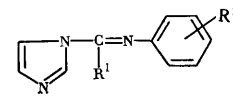
It is important to note that the introduction of bulky substituents into the ligand molecule frequently diminishes the number of coordinated groups. However, when the substituents are remote from the coordination centre, the composition of the complexes is the same as for the unsubstituted molecule. Thus *N*-alkylimidazoles form complexes having the composition MX_2A_6 even in the presence of the butyl substituent, while compounds containing not more than four ligand molecules can be isolated for 2-methyl- and 1,2-dimethyl-imidazoles.[66-69]

The same phenomenon occurs in the synthesis of imidazole complexes with pesticidal activity. Thus the complexes of Cu^{2+}, Mn^{2+}, Fe^{2+}, Ni^{2+}, Ca^{2+}, and Mg^{2+} chlorides with carbamoyl imidazoles contain between two and four ligand molecules:



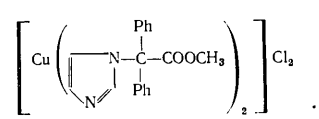
R^1 = alkyl; R^2 = phenoxyalkyl.

On the other hand, the interaction in an inert organic solvent of imidazole derivatives of the type

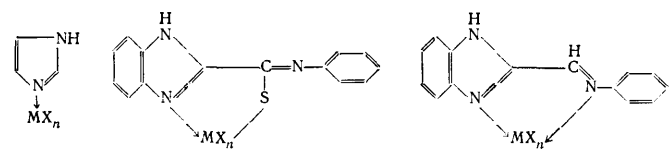


(R^1 = alkyl, alkoxy-group, or $PhCH_2$; R^2 = Cl or CF_3) with Cu^{2+}, Zn^{2+}, Mn^{2+}, Co^{2+}, Fe^{2+}, and Al^{2+} sulphates, chlorides, acetates, and nitrates leads to the formation of complexes containing only two or three ligand molecules.[160-166]

The nature of the metal has little influence on the composition of the complexes. Only copper salts, for which it is not always possible to isolate complexes containing six molecules of azole ligands, are an exception. Thus, the copper complex of methyl diphenylimidazole-1-acetate, which is obtained by the reaction of the ligand and $CuCl_2$ in an alcoholic medium, contains only two molecules of the imidazole derivative:[167]



The question of the location of the coordinate bond is important for imidazoles, benzimidazoles, and their substituted derivatives. Depending on the type of molecule, the metal, and the conditions of synthesis, the coordinate bond can be located at the "pyridine" N(3) atom, or at another heteroatom (O or S) present in the substituted molecule, or in the π-electron system:



According to the literature data discussed by Garnovskii and co-workers,[61,62] coordination takes place predominantly via the nitrogen atom of the "pyridine" type. In this case the molecules of imidazoles and benzimidazoles play the role of monodentate ligands.

The same conculsion concerning the location of the bond in imidazole *N*-ethylimidazole, and *N*-propylimidazole biologically active complexes of Mn^{2+}, Pt^{2+}, and Pd^{2+} was arrived at by other investigators.[77-82]

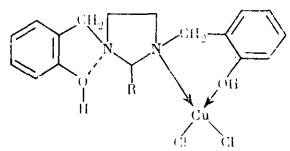
A number of studied have been devoted to metal complexes with 1-vinylimidazoles (A), including those exhibiting biological activity.[83-85] It has been shown by ^{13}C NMR that the coordination of the ligand in the complexes of vinylimidazoles with tin halides $R_{4-n}SnX_n.nA$ (R = alkyl; *n* and *m* = 1 and 2) takes place via the "pyridine" nitrogen atom, which

can entail a change in the mutual orientation of the vinyl group and the heterocycle. The same mode of addition of the ligand obtains in the complexes $MX_n.2A$ and $MX_n.4A$, where MX_n represents Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, and Al^{3+} halides. However, Shchelokov et al,[86] who investigated the Pt^{2+} and Pd^{2+} complexes with 1-vinylimidazole, reached the conclusion, on the basis of infrared spectra, that the vinyl group can be involved in the formation of a bond with the central atom.

2-Hydroxymethyl-1-vinylimidazole, 1-vinyl-2-vinyloxymethylimidazole, 1-ethyl-2-vinyloxymethylimidazole, as well as their benzimidazole analogues have been used as ligands.[87,88] Complexes with the halides, sulphates, and acetates of a series of transition metals have been isolated. Their composition ranges form 1:1 to 1:4 (M:A). The chlorides and acetates show respectively the highest and lowest coordinating capacities. The presence of a substituent in the 2-position in the imidazole ring leads to the formation of complexes in which the metal is coordinated to a smaller number of ligands than in the case of unsubstituted 1-vinylimidazole.

Spectroscopic data have shown that the hydroxymethylimidazoles are coordinated via the nitrogen atom in the 3-position in the imidazole ring. The coordination interaction involves also the π-electron system of the heterocylce and the vinyl group.

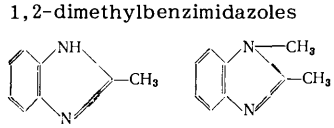
Metal complexes with imidazolidine derivatives have been described.[89,90] Compounds containing not more than two ligand molecules, whose bonds with the central atom are formed via a nitrogen atom as well as the atoms of other functional groups present in the molecule, are produced, for example:



R = Ph, $C_6H_4OCH_3$, CH_3.

In surveying the studies of recent years on the synthesis and properties of complexes of benzimidazole and its substituted derivatives,[91-96] one may note the rarely encountered case where the bond between the benzimidazole ligands and the complex-forming agent in the mixed copper(II) carboxylate complexes with benzimidazole $CuZ.HA.H_2O$ (HA = Benzimidazole and Z = residues of malonic, succinic, malic, or maleic acid) is believed[91] to be formed via the nitrogen atom of the NH group, whose stretching vibration frequency undergoes a bathochromic shift on coordination.

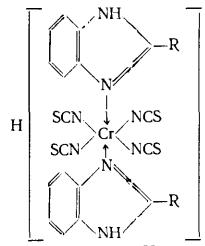
On the basis of the bathochromic shift of the ν(CN) stretching vibration frequency of the imidazole ring on coordination, it has been concluded that the molecules of benzimidazole derivatives in the complexes of bivalent zinc and manganese with 2-methyl- or 1,2-dimethylbenzimidazoles



(HA) (A')

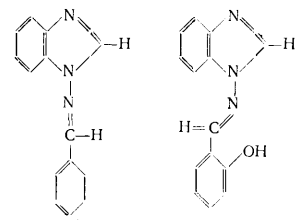
having the compositions $MX_2.HA$ and $MX_2.2A'$ (X = Cl, Br, I, NO_3, CH_3COO, or $1/2SO_4$) add to the zinc(II) and manganese(II) ions via the nitrogen atom in the 3-position in the imidazole ring. The spectra of the complexes can also contain bands characteristic of the acid residues present in the inner sphere.

In the chromium(III) complexes of 2-ethyl and 2-propylbenzimidazoles which have been isolated, the *N*-coordination of the thiocyanate groups has also been indicated:



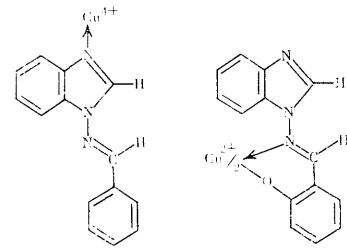
R = C_2H_5, C_3H_7

After the interaction of copper(I) halides and acetates with benzylidene-1-aminobenzimidazole (A') and salicylidene-1-amino-benzimidazole (A"),



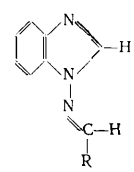
(A') (A")

complexes of two types were isolated: the molecular adducts CuX.A', $2CuAc_2.3A'$, CuX.A", and CuX.3A", as well as the inner complex $Cu(A'' - H)_2$, where X = Br or I. It has been shown by infrared spectroscopy that the azomethines are coordinated to the copper(I) atom via the nitrogen atom of the "pyridine" type in the benzimidazole ring in the molecular adducts and via the azomethine group in the inner complex, for example:



A study of the EPR spectra of the complexes obtained has shown that the interaction of the azomethines (A') and (A") with copper(I) halides is not accompanied by a change in the valence state of copper in the case where complexes of the type of adducts are formed. The interaction involving the formation of the inner complex leads to the formation of bivalent copper complexes and CuBr is oxidised more readily than CuI.[97]

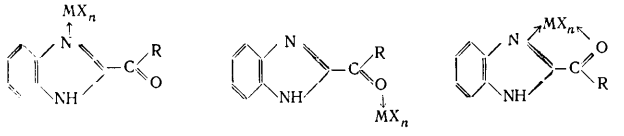
The complex-forming properties of the azomethines of 1-aminobenzimidazoles are determined by the specific features of the steric and electronic structures of the ligand. It has been established that the coordination interaction of the azomethines of 1-aminobenzimidazoles with metal salts proceeds in the first place via the N-donor centre of the hetero-fragment and not via the azomethine bond $-N = C\lesssim$:[98]



R = Ph, $C_{10}H_7$, 3-IC_6H_4, 3-$NO_2C_6H_4$, 4-$NO_2C_6H_4$, 2-HOC_6H_4, 3-BrC_6H_4, 5-BrC_6H_4, 4-HOC_6H_4.

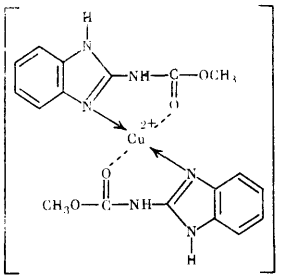
Transition metal complexes with 2-(2-hydroxyphenyl)- and 2-(2-aminophenyl)benzimidazoles contain one or two ligand molecules. It has been shown by infrared spectroscopy that the aminophenyl derivative of benzimidazole is coordinated via the amino-group of the aniline residue and the tertiary N(3) atom of the imidazole ring. In the complexes of 2-pyridylbenzimidazoles with lanthanides and molybdenum(III) coordination is achieved via the nitrogen atom of the pyridine ring and the N(3) atom of the imidazole ring.[99-106]

In the complexes with carbonylbenzimidazoles the coordinate bond is located predominantly at the nitrogen atom of the heterocycle and complex formation proceeds via the oxygen atoms only in the case of the "hardest" Lewis acids:[61]



R = H, alkyl .

Copper(II) complexes with methyl benzimidazole-2-carbamate (HA) have been described.[107] A product having the composition $CuX_2.2HA$ (X = Cl or Br) was obtained. The infrared spectrum of the ligand contains in the region of the stretching vibrations of the NH group a single band at 3300 cm^{-1}. The stretching vibration band of the carbonyl group is at 1710 cm^{-1} and $\nu(C=N)$ is at 1630 cm^{-1}. There is hardly any change in the position of the 3300 cm^{-1} NH vibration band in the spectrum of the complex, although its intensity is appreciably reduced. The vibration bands of the carbonyl and C = N groups are at 1735 and 1645 cm^{-1}. On this basis, it has been suggested that the bond with the metal ion in the complex is formed via the tertiary nitrogen atom and the carbonyl oxygen atom:



As stated in previously published reviews,[61,62] the type of polyhedra formed in the complexes with azoles depends on a series of factors: the coordination number and the electronic configuration of the complex-forming agent, the character of the anion, the nature of the ligand, and in some cases also the state of aggregation of the system. The configuration of the complexes with imidazoles and benzimidazoles was usually determined from magnetic susceptibility and spectroscopic data. Studies on the X-ray diffraction of such compounds are more rarely encountered.

It has been shown on the basis of the observed effective magnetic moments at different temperatures, spectroscopic data, and electrical conductivity in methanol that the complexes with 4-methylimidazole (HA) having the composition $[M(HA)_6]X_2$ [M = Co(II) or Ni(II)] and also $[Ni(HA)_6].[HgCl_4]$, $[Ni(HA)_2(NCS)_4]^{2-}$ and $[Ni(HA)_4(NCS)_2]$ have an octahedral or distroted octahedral configuration, while the complexes $[Ni(HA)_2Cl_2]$ and $[Ni(HA)_4X_2]$ have a tetrahedral configuration. The thiocyanate group in the inner sphere is present in the form of an ion coordinated to the nitrogen atom, which plays the role of a bridge.[108] An X-ray diffraction study of the compound CoA_2Q_2, where A = 1-methylimidazole and Q = 2,4,6-trichlorophenol, showed that Co^{2+} is located in a distorted tetrahedral environment made up of the nitrogen atoms of the two A ligands and the oxygen atoms of the two Q ligands. In view of the bond between the metal ion and one of the chlorine atoms of the Q ligand, the environment of the metal becomes of the distorted square-pyramidal type with one of the nitrogen atoms at the apex of the pyramid. The structure is stabilised by two intramolecular hydrogen bonds C–H...Cl between a carbon atom of A and a chlorine atom of Q. For the same ligands in the Co^{2+}, Zn^{2+}, and Ni^{2+} complexes, it has been found by spectrophotometric and EPR methods that the Q anion in MQ_2A_n is linked to the central atom and the complexes have the configuration of a distorted tetrahedron or a distorted octahedron.[109,110]

The structure of $[CuA_4(AcO)_4].6H_2O$ consists of centrosymmetric dimers linked by acetate bridges. The copper atom is involved in a tetragonal-pyramidal coordination with one bridging acetate ligand at the apex of the pyramid and with the nitrogen atoms in the two methylimidazole ligands and the oxygen atoms of the acetate ions at the base of the pyramid. Water molecules form a system of hydrogen bonds.[111]

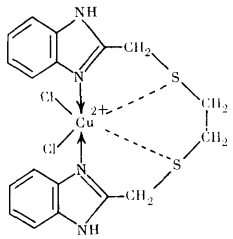
On the basis of X-ray diffraction data and the results obtained by other physical research techniques, it has been established that the copper complexes of 1-methylimidazole and substituted iminoacids have a square-planar structure. The copper atom is located at the centre of symmetry and is surrounded by the two oxygen atoms of the carbonyl groups and two nitrogen atoms of the substituted imidazole. On coordination of two water molecules, the complex has a distorted octahedral configuration.[112,113]

Rhodium complexes containing imidazole (HA^1), benzimidazole (HA^2), and 2-methylbenzimidazole (HA^3) with the compositions $[Rh(HA^1)_4Cl_2]Cl$, $[Rh(HA^2)_4Cl_2]Cl$, $[Rh(A^2)_3].3H_2O$, and $[Rh(HA^3)_4(H_2O)_2]Cl_3$, as well as the iridium compounds $[Ir(HA^2)X_3(H_2O)_2]I$ (X = Cl, Br, or I) and $[Ir(HA^2)_4X]X$ (X = Br, I, NO_2, or NCS), have a polymeric octahedral structure with bridging groups. On the other hand, the complexes $[Pt(HA^3)_4]Cl_2$, $[Pt(HA^1)_2Cl_2]$, $[Pt(HA^2)_2Cl_2]$, and $[Pt(HA^3)_2Cl_2]$, as well as compounds in which the chloride ion has been replaced by the Br^-, I^-, and NO_3^- ions are monomeric and have a planar *trans*- or *cis*-configuration.[114]

The complexes coordinating between four and six 2-methylbenzimidazole molecules have a distorted tetrahedral configuration for Cu^{2+}, a tetrahedral configuration for Co^{2+}, and an octahedral or tetrahedral configuration for Ni^{2+} and Fe^{3+}.[115] The nickel compounds $[Ni(HA)_4]X_2$ (X = Cl, Br, or NO_3 and HA = benzimidazole and its derivatives) have a square-planar structure. On heating, the chloride, bromide, and nitrate complexes are converted into $[Ni(HA)_4]X_2$ and the values of μ_{eff} indicate the formation of a distorted octahedral configuration. The replacement of the benzimidazole derivative by the unsubstituted ligand makes it possible to achieve such a transition also for the iodide compounds.[116]

X-Ray diffraction and electronic spectroscopic data as well as measurements of the magnetic susceptibility have shown that the Co^{2+}, Ni^{2+}, and Cu^{2+} complexes of 5-nitrobenzimidazole have pseudotetrahedral and distorted octahedral structures. The cobalt and halogen-containing nickel compounds with 3,4-dihydro-1-phenyl-1*H*-1,4-oxazino[4,3*a*]benzimidazole have a tetrahedral configuration. On the other hand, the nickel(II) thiocyanate complex is square planar. In all the compounds indicated the ligand is coordinated via the N(3) atom of the benzimidazole ring. In the copper complexes of

tris(2-benzylimidazolymethylamine) there is a trigonalbipyramidal or distorted octahedral configuration. The study of the structure of the complex



showed that the copper atoms are located in a distorted trigonal-bipyramidal environment with the N(3) atom of the ligand in the axial position and also with two S atoms and Cl^- ions in the equatorial plane.[117-120]

The stability of the complexes of azoles had not been the subject of systematic study previously. There were only isolated investigations of the stability of imidazole compounds. The stability of the complexes is directly related to their biological activity. It follows from Azizov's study[5] that complexes with an average stability constant $\lg \beta \cong 8-9$ exhibits the highest bioactivity. Numerous publications devoted to the investigation of the thermodynamic and kinetic stabilities of coordination compounds with imidazole, benzimidazole, and their substituted derivatives have appeared recently. Thus the relative basicities of imidazole and its substituted derivatives have been estimated[121-125] and studies have been made of the complex formation reactions of cobalt(II), copper(II), and nickel(II) salts with the above ligands. It follows from the values of pK_B found for the ligands in benzyl and n-butyl alcohols that the electron-accepting properties of the imidazoles become more pronounced with enhancement of the acid properties of the alcohols. In DMSO, acetonitrile, and acetone the differences between the proton-accepting properties of the ligands in each solvent depend mainly on the inductive effect of the substituent, on which steric effects associated with the number, size, and degree of branching of the substituents in the imidazole molecule may be superimposed. When electron-donating substituents are introduced into the ligand molecule, an increase of the stability of the Co^{2+} and Cu^{2+} complexes is observed, while the introduction of the electron-accepting substituents entails some decrease of the stability of the complexes. The study of the complex formation reaction between Ni^{2+} and imidazoles demonstrated a decrease of the rate of formation of the complex in the presence of small amounts of added acetone, which can be accounted for by the specific solvation of the ligand and by a change in the dielectric constant of the medium.

The presence of the hydroxide ion influences the formation of complexes by the Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, and Hg^{2+} salts with imidazole (HA). At low ligand concentrations the complex $M(OH)_2.HA$ is formed, while at high concentrations the complex $M(HA)_n$ ($n = 1-4$) is formed stepwise.[126-130]

The study of the formation of mixed complexes with imidazole and aminoacids showed that Zn^{2+} reacts with imidazole, histamine (H_2R), and histidine (H_3Q) to form the complexes $[Zn(HA)_n]^{2+}$ ($n = 1-4$) and also $[Zn(HA)_nR]$ ($n = 1$ or 2) and $[Zn(HR)Q]^{2-}$ and $[Zn(H_2R)Q]^-$. The composition of the complexes shows that imidazole is coordinated as a monodentate ligand without the elimination of a proton while histamine and histidine are coordinated as bi- and tri-dentate ligands with abstraction of one, two, or three protons.[131-134]

The dissociation constants of the ligands and the stepwise stability constants of the Cu^{2+}, Co^{2+}, Ni^{2+}, and Zn^{2+} complexes with 4-methylimidazole (HA) have been determined. In the case of Co^{2+} in aqueous solution there is an equilibrium between the octahedral complexes $[Co(H_2O)_{6-n}(HA)_n]^{2+}$ and the tetrahedral compounds $[Co(H_2O)_{4-n}(HA)_n]^{2+}$. The dependence of the formation constants K_n on the number of coordinated ethylimidazole molecules n for Cu^{2+} and Zn^{2+} is anomalous in the case of K_3 and K_4. In this case the logarithms of the constants are equal to the sums of the corresponding quantities for the complexes $[M(HA)_4]^{2+}$, $[M(H_2O)_2(HA)_2]^{2+}$, and $[M(H_2O)(HA)_3]^{2+}$ formed simultaneously in solution.

The stability constants ($\lg \beta_n$) show that the stability of the complexes of methylimidazole is somewhat lower than that of the corresponding compounds of the butyl derivative as a consequence of the lower basicity of methylimidazole. The stability of the complexes of Co^{2+}, Ni^{2+}, and other transition metals with 1-methyl-, 2,2-dimethyl-, 2-ethyl-, 1-methyl-, 2-ethyl-, 1,2,4-trimethyl-, 1-propyl-, and 1-butyl-imidazoles diminishes with increase in the size of the substituent in the imidazole molecule. In the complex formation reaction of the transition metals with imidazole derivatives having involved substituents, 1:1 complexes are formed as a rule. Thus 2-[(2-carboxyphenyl)azo]-4,5-diphenylimidazole reacts with Th^{4+}, UO_2^{2+}, and Ce^{3+} ions in ethanol to form compounds with the composition indicated and stability constants, $\lg \beta$, 7.17, 6.91, and 6.68 respectively for these ions.[135-143]

A number of studies have been devoted to the complex formation reactions of transition metals with benzimidazole and its substituted derivatives. It has been noted[144-146] that the formation of complexes by copper(II) and cobalt(II) chlorides and nitrates in non-aqueous solutions is influenced by the nature of the solvent and to a lesser extent by the size and character of the substituent in the benzimidazole molecule. In the case of cadmium(II) carboxylates the stability of the complex with benzimidazole depends on the charge of the complex species. The addition of the first benzimidazole molecule to the complex cation is less favourable than the interaction with the uncharged species. This is associated with the change in the strength of the dative $d-\pi^*$ bond between the metal carboxylate and benzimidazole. A π-dative interaction has been noted in the formation of complexes by substituted benzimidazoles with Co^{2+}, Zr^{2+}, Ni^{2+}, and Mn^{2+}. Benzimidazole and 4-azobenzimidazole form the complexes $[M(H_2O)_{6-n}(HA)_n]^{2+}$, while 2-hydroxymethylbenzimidazole forms the complexes $[M(HA)_4]^{2+}$.[147-149]

Summarising the literature data presented for the metal complexes of imidazoles and benzimidazoles, one may conclude that the azole complexes isolated from solutions or melts contain between one and six ligand molecules. The coordinate bond is as a rule located at the "pyridine" nitrogen atom and other heteroatoms in the substituted azole molecule and is involved in complex formation only in the case of "hard" Lewis acids.

The type of polyhedra of the transition metal complexes of imidazole, benzimidazole, and their derivatives depends on a number of factors. The data presented lead to the conclusion that the geometrical configuration of the complexes with azoles varies from distorted octahedral to square planar. The nature of the complex-forming agent and the ligand as well as the character of the anion of the metal salt are very important in this instance.

In considering the stability of the complexes of azoles in solution, one may note its decrease with increase in the size of the substituent in the ligand molecule. The stability is influenced by the inductive and steric effects of the substituents in the azole molecule and also by the nature of the organic solvent (the majority of studies on the formation of complexes by imidazoles and benzimidazoles have been performed in a non-aqueous medium). In the series of benzimidazole complexes the stability is influenced also by the π-dative

interaction involving the *d* electrons of the metal and the antibonding π* orbitals of the ligand molecule.

IV. BIOLOGICAL ACTIVITY OF COMPLEXES OF LACTAMS, IMIDAZOLES, AND BENZIMIDAZOLES

The study of the biological activity of complexes is important for medicine and agriculture. Investigation of the properties of these substances in biological cycles of toxic elements and in the first place in their interaction with various organisms in the environment (bacteria, fungi, higher plants, and animals) plays an important role.

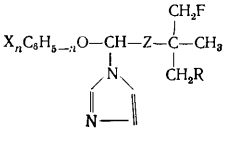
The use of biocoordination compounds in medicine is based on the fact that the concentration of biometals in various tissues for the normally functioning organism must be maintained at vigorously specified levels by regulating them with the aid of the system of appropriate proteins and hormones. In some cases it is necessary to resort to special preparations containing the particular bioelement in a form assimilable by the organism.[2]

Biocoordination compounds as chemical plant protecting agents have been attracting increasing attention in the agricultural industry. This is because the metal-containing organic compounds exhibit a high activity against a broad spectrum of pathogens and are as a rule safe for the environment.

The question of the physiological activity of coordination compounds of lactams and azoles has been inadequately investigated. The metal complexes of azoles play an important role in biological objects and processes.[150-152] The imidazole group enters into the composition of the most important enzymes: creatine kinase, chymotrypsin, carboxypeptidase A, carboanhydrase B, and others. The imidazole group is very important in phosphorylation systems. Haemoproteins fulfil an important biological role. The involvement of the imidazole group of histidine in the binding of oxygen by haemoglobin and myoglobin has been postulated.

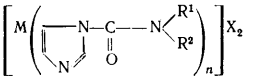
Metal complexes with imidazole, benzimidazole, and their derivatives possess pharmacological activity. Stimulators of antitumour protection, preparations with antimicrobial activity, etc. have been found among them.[81,85]

Such compounds include platinum(II) and palladium(II) complexes of 1-ethyl- and 1-propyl-imidazoles having the composition MX_2A_2 and MX_2A_4 (X = Cl, Br, or I). The complexes of many transition metals with imidazole derivatives having the general formula

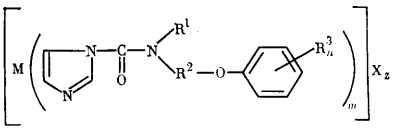


where Z = CO or CH(OH), R = H or F, X = halogen, alkyl, NO_2, CN, alkoxycarbonyl, substituted phenyl, or unsubstituted phenyl, and n = 0–3 can be used in medicine and veterinary practice for the treatment of dermatomycoses and systemic mycoses. The cobalt(II) and nickel(II) complexes containing two or four molecules of 3,4-dihydro-1-phenyl-1*H*-oxazino[4,3*a*]benzimidazole possess antiviral properties.[153-156] There are some data concerning the pharmacological activity of the metal complexes of lactams.[157-160] Thus, certain 1,5-disubstituted pyrrolidinones and their salts exhibit vasodilating, antiulcer, and hypotensive activities. Lactam derivatives, in particular silylated lactams, have attracted attention as valuable physiologically active substances. They function as mediators in the inhibition of the nervous system and posses anticonvulsant, [illegible]

Many metal complexes with imidazole, benzimidazole, and lactams exhibit a pesticidal activity. Thus carbamoylimidazoles and their complexes with copper(II), manganese(II), iron(II), calcium(II), nickel(II), and magnesium(II) salts are active fungicides:

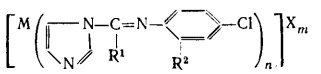


(R^1 = alkyl, R^2 = phenoxyalkyl, X = univalent anion, and n = 2–4) and



(R^1 = alkyl, R^2 = branched alkylene, R^3 = alkyl or halogen, n = 0–5, m = 2 or 4, and X = univalent anion). At a concentration of 1 g litre^{-1} the preparations inhibit the development of *Botrytis cinerea* and *Erysiphe graminis*.[160-162]

The copper(II), zinc(II), manganese(II), cobalt(II), iron(III), and aluminium(III) compounds

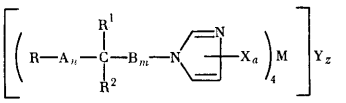


(R^1 = alkyl, alkoxyalkyl, or $PhCH_2$, R^2 = Cl or CF_3, n = 2 or 3, X = univalent anion, and m = 2 or 3) exhibit a broad spectrum fungicidal activity.

The complexes and the ligands entering into their composition can also possess plant growth stimulating properties, apart from their fungicidal activity. At a concentration of 4 g litre^{-1}, they influence the growth of soya, tomatoes, the cottonplant, etc., they intensify the green colour of leaves and bushing out, and inhibit apical tissues.[163-166]

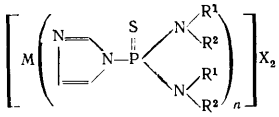
The copper complex of methyl diphenylimidazole-1-acetate (A) $[Cu(A)_2]Cl_2$ is a fungicidal preparation (especially active against powdery mildew fungi). At a concentration of 1.2×10^{-4}–1×10^{-9}% the preparation greatly reduces the infection of barley by the fungus *Erysiphe graminis*, the infection of the apple tree by *Podosphaera lencotricha*, and of cucumbers by *Erysiphe cichoreaclarum*.[167]

The calcium(II), magnesium(II), manganese(II), copper(II), zinc(II), nickel(II), cobalt(II), tin(II), cadmium(II), chromium(III), and iron(III) complexes of 1-arylalkylimidazoles possess fungicidal activity:[168-171]



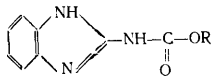
(R = aryl or substituted aryl, R^1 and R^2 = alkyl, alkenyl arylakyl, substituted arylakyl, phenyl, substituted phenyl, etc., A and B = alkylene, X = alkyl, halogen, or NO_2, a = 0–3, n and m = 0 or 1, and Y = anion). In contrast to the free imidazoles, the complexes are not phytotoxic, can be used to treat green plants, and also can serve as seed pickling agents. They suppress the development of phytopathogenic fungi and are effective against barley *helminthosporiosis*, the grey mould and mildew of the leguminous plants, tomatoes, and the grape vines, phytophtorosis of tomatoes, piriculariosis of rice, and the stem and grey rust in wheat.

The cobalt(II), cadmium(II), iron(II), nickel(II), manganese(II), and zinc(II) complexes of imidazolylphosphonothioic diamide, i.e.

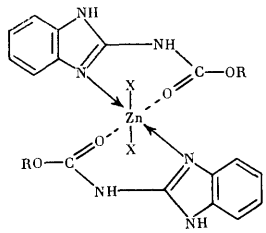


where R^1 and R^2 = alkyl, Ph, CH_2CHCH_2, CH_2Ph, or furfuryl, X = non-phytotoxic anion, and n = 1–4, possess fungicidal activity. The compounds can be used as bactericides for the protection of plants and also various materials (polymers, fabrics, and paper).[172–174] At a concentration of 24–100 mg litre^{-1}, the complexes induce 75–100% destruction of *Phytophtora infestans*, *Venturia inaequalis*, and other fungi.

Transition metal complexes of benzimidazole derivatives have been investigated as effective fungicides. The zinc(II) and copper(II) complexes of urethanes

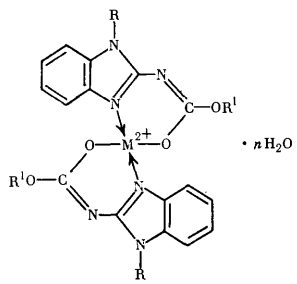


where R = lower alkyl, have been described in patents,[175–178] for example:



The complexes exhibit protective and eradicating fungicidal activities. At a concentration of 16–80 mg litre^{-1} they are active against apple scab and powdery mildew. A number of transition metal complexes of methyl benzimidazole-2-carbamate exhibit a broad spectrum of fungicidal activities, are non-toxic to man, and their fungicidal activity persists for a long time. The preparation can be used for the protection of plastics and leather.

Fungicidal and acaricidal activities are shown by the cadmium(II), zinc(II), copper(II), nickel(II), manganese(II), and cobalt(II) complexes having the general formula

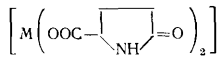


where R = $-\overset{O}{\overset{\|}{C}}-NHR^2$; $-\overset{O}{\overset{\|}{C}}-R^3$, $-\overset{S}{\overset{\|}{C}}-CCl_3$ (R^1 = alkyl, R^2 = alkyl or substituted alkyl, etc. R^3 = H, alkyl, alkenyl, cycloalkyl, phenyl, etc., n = 0–3[179,180]). Dehydration of the compounds leads to an increase of their fungicidal activity and also to an appreciable improvement of stability on storage.

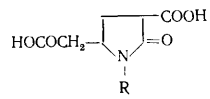
Mixtures exhibiting a synergistic effect are also employed as fungicidal preparations. They contain zinc salts and methyl 1-butylcarbamoylbenzimidazole-2-carbamate. They readily penetrate plants and exhibit a prolonged protective activity. Fungicidal preparations containing a mixture of methyl benzimidazole-2-carbamate and the manganese or zinc salt of ethylenebisdithiocarbamic acid in proportions ranging from 1:1 to 1:20 (1:10 are the preferred proportions).[181]

Less information is available in the literature about the pesticidal activity of lactam complexes. The use of coordination compounds of lactams agains plant pathogens has been reported.[182–186] The substances proved to be effective inhibitors of the growth of certain phytopathogenic bacteria inducing diseases of the grapevine and certain melon crops. In particular, they inhibit the growth of *Bacterium tumefaciens*, *Pactobacterium aroideae*, and *Xanthomonas campestris*.

Complexes based on 5-alkyl-1-(β-aminoethyl)-2-pyrrolidinones, described by Sedavkina and Shebaldova,[22] exhibit antimicrobial and antiphage activities. The parmacological and pesticida' activities of pyrrolidinonecarboxylic acids have been mentioned.[53–60] The zinc(II), copper(II), and calcium(II) complexes



show an antifungal effect. The zinc salt shows a greater inhibiting activity against dermatophytes than the copper salt. On the other hand, the calcium salt influences protein metabolism in bony and skin tissues. Fungicidal preparations containing only the copper salt of the amidodicarboxylic acid



(R = H, alkyl, or cycloalkyl) are especially effective against phytophtorosis and the genuine powdery mildew of cucumbers.[58]

Among the lactam complexes of transition metal salts, the preparation "Kartotsid" [Cartocide?] the copper(II) complex of ε-caprolactam exhibiting a broad spectrum of fungicidal acitivity and safe for the environment, is promising.[187] It can replace the familiar fungicidal preparations, namely copper oxide chloride and Khomezin—in sugar beet and potato plantations, vineyards, and orchards, and also makes it possible to reduce appreciably the consumption of copper.[188] Furthermore, the preparation has a low toxicity (LD_{50} = 1200 mg kg^{-1}) for warm blooded animals.

When biologically active metal complexes are used, it is very important to investigate the mechanism of their action on living cells. The character of the action of biocoordination compounds is at present by no means always clear. There exist at least three possible mechanisms of their action: (1) the activity is manifested by the ligand and the role of the metal reduces to creating a suitable transport form; (2) the metal ion itself exhibits an activity and the complex is necessary for the transport of the metal ion across the cell membrane; (3) the active species, namely the complex ions, can interact with cell centres important for vital activity.[2]

The majority of the theories of the mechanism of the action of copper-containing preparations are based on the adsorption capacity of the fungal cell protoplasm. It is known that a deposit of the copper-containing fungicides on the plant is not absolutely insoluble in water—a certain microamount of copper is present in solution. According to the cumulative theory, the copper present in solution is absorbed by the spores, which disturbs the equilibrium and fresh portions of copper dissolve. The process continues until the sport accumulates a toxic dose of copper.[189]

In certain cases the fungicidal properties of copper complexes can be explained by their structure. Thus the free coordination site in the *trans*-position relative to the chlorine atom is not fully shielded in the compound having formula(II) and described in patents[35-38] (see above), where the ligand is caprolactam and the inorganic salt is $CuCl_2$. Precisely this fact can explain the high biological activity of the compound. Probably owing to the imperfection of the coordination environment of the copper atom, the latter interacts with the sulphhydryl groups of enzymes and coenzymes, since the latter are especially sensitive to the action of heavy metals. This leads to the precipitation of the protein substance, as a result of which the fungus is destroyed. However, the available data about the behaviour of complexes in bio-objects are as yet inadequate for an unambiguous solution of the problem of the mechanism of the action of these complexes.

In order to determine the mechanism of the action of the fungicidal preparation "Kartotsid", a study has been made of its interaction with two-layer phospholipid membranes,[190] since transfer across a two-layer membrane is decisive in the action of any physiologically active susbstance. It is known that two-layer lipid membranes are effective models of cell membranes. Measurements of the membrane potential, electrical resistance, and electrical capacitance of lipid two-layer membranes as a function of the "Kartotsid" concentration suggested that the primary mechanism of its fungicidal action is associated with the increase of conductivity and with the breakdown of the structural organisation of the cell membrane. The increase of the membrane conductivity is caused by the lipophilic properties of the membrane-active form of "Kartotsid". The molecules of the preparation in living organisms apparently act not only on the surface regions of the cell membranes but also penetrate into the interior of the cell.

As a result of their penetration into the cell, the copper ions inactivate enzymes, forming chelate complexes. The activity of many enzymes is known to diminish following the substitution of the active metal of the enzyme complex (for example, magnesium) by heavy metals such as copper or mercury. Thus the role of the lactam molecules in the complex with the copper ion probably reduces to facilitating the transmembrane transfer of Cu^{2+} ions into the interior of the cell.

Summarising the data presented concerning the physiological activity of imidazole, benzimidazole, and lactam complexes, one may conclude that at present they have not as yet found a wide-scale application in the national economy, although much work is already being done along these lines. Evidently many transition metal complexes of the above ligands possess pesticidal and pharmacological activities. In most instances the activity of the complexes is higher than that of their constituent organic molecules. Furthermore, the complexes are always less toxic for warm blooded animals than the coordinated physiologically active ligands. It has been shown in relation to the preparation "Kartotsid" that bio-coordination compounds contain less toxic copper than the preparations based on simple copper salts used at present which is extremely important from the ecological standpoint. All these factors make one confident that physiologically active metal complexes will find more extensive applications in agriculture in the immediate future.

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The Synthesis and Luminescence-spectroscopic Properties of Fluorescent Condensation Polymers

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The results of studies on the synthesis of polycondensation phosphor-containing aliphatic and aromatic polymers as well as the products of polymer-analogue transformations with phosphor-groups in the side chain are examined. The light absorption and luminescent properties of the polymers obtained and of model compounds having an analogous structure are discussed. The bibliography includes 108 references.

CONTENTS

I. Introduction 690
II. Aliphatic polycondensation polymers 690
III. Products of polymer-analogue transformations 696
IV. Aromatic fluorescent polymers 699

I. INTRODUCTION

Numerous studies on the synthesis and spectroscopic properties of fluorescent polymers have been published in recent years. However, the available results have not so far been the subject of a suitable survey in the Soviet literature. Foreign reviews deal only with data on the synthesis and spectroscopic properties of polymerisation phosphor-containing polymers.[1-3] Nevertheless the knowledge of the luminescence-spectroscopic properties of such polymers, obtained both by polymerisation and polycondensation, is of great theoretical importance in view of the possibility of investigating intramolecular and intermolecular electronic energy transfer and migration processes in a polymeric medium and is of definite practical interest, because the fluorescent properties of polymers are closely related to their photoconducting characteristics and resistance to the action of light.

In recent years a number of trends have arisen in technology which utilise the capacity of certain polymers for intense fluorescence. These include in the first place the preparation of daylight fluorescent pigments on a polymeric base and of plastic scintillators[4] as well as polymeric active elements for laser technology.[5]

In the present review an attempt is made to survey the available literature data on the synthesis and spectroscopic characteristics of aliphatic and aromatic phosphor-containing condensation polymers.

II. ALIPHATIC POLYCONDENSATION POLYMERS

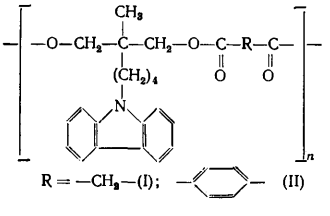
It is known[6-8] that many of the natural polycondensation polymers (proteins) glow in the range 280–360 nm as a result of the emission of light by aromatic aminoacid residues—those of tryptophan, tyrosine, and phenylalanine. Synthetic polycondensation polymers [of the type of polycaprolactam and poly(ethylene terephthalate) containing chromophoric groups in the chain], which have a bright colour and apparently fluoresce, were first obtained by Bykov and co-workers at the beginning of the 1960's.[9-12] Data obtained in these and similar investigations have been surveyed in a review.[13]

Concentrating on later investigations, we may note that the ability of polycondensation polymers to fluoresce has been usually imparted by introducing into the composition phosphor fragments related to carbazole, anthracene, pyrene, or other condensed aromatic or heteroaromatic nuclei. We shall consider polymers of each of these types.

1. Carbazole-Containing Polymers

Carbazole-containing polymers, obtained by polarisation methods, in particular polyvinylcarbazole, are promising materials for electrophotography, which is based on the phenomenon of the photoeffect in electrically charged high-resistance films.[14] Cheap electrophotographic layers, whose sensitivity is close to those made from inorganic photoconductors, can be obtained on the basis of such polymers.[15] According to Voishchev et al,[16] certain polycondensation carbazole-containing polymers, which have been described in fair detail in the literature,[17] also exhibit a high photoconductivity. However, the luminescence-spectroscopic properties of such materials have been investigated less fully than those of polyvinylcarbazole and related compounds.[1] Thus the synthesis of fluorescent polyesters[18-20] and polyurethanes[21] with ω-9-carbazolylbutyl groups, as well as polyamides based on 3,6-diamino-9-ethylcarbazole[22] has been described in a series of reports by Tazuke and co-workers.

The polyesters (I) and (II) have been obtained by the polycondensation of 6-carbazolyl-2,2-dihydroxymethylhexane with the diethyl esters of dicarboxylic acids at 150–160 °C for 3 h in a nitrogen atmosphere and then *in vacuo* for 10 h:[18,19]



The light absorption and fluorescent properties of the polymers (I) and (II) have been investigated simultaneously with the properties of the model compound (III) (Fig.1), which is a product of the condensation of 6-carbazolyl-2,2-dihydroxymethylhexane with ethyl acetate. Fig.1*a* shows that the absorption properties of the polymers (I) and (II) are similar in the range $\lambda > 270$ nm, where the only

light absorbing group is the carbazolyl group. The differences in the range $\lambda < 270$ nm are associated with absorption by the terephthalate unit. The fluorescence spectra of the polyester (I) and of the model compound (III) are identical and contain only the monomer fluorescence band with $\lambda_{max} = 368$ nm. On the other hand, an additional broad structureless exciplex band with $\lambda_{max} = 490$ nm appears in the fluorescence spectrum of the polyester (II). The intensity ratio of the exciplex and monomer fluorescence bands† I_e/I_m depends on the degree of polycondensation n[19] and diminishes when the solution is diluted. The latter finding indicates the operation of an intermolecular mechanism of the formation of the exciplex even at a concentration of 10^{-4} M.[18]

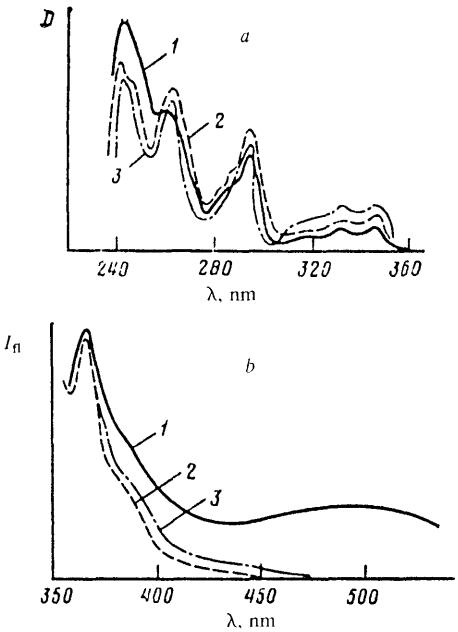
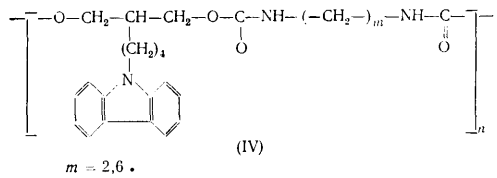


Figure 1. Absorption (*a*) and fluorescence (*b*) spectra of dioxan solutions of the polymers (II) (curve *1*) and (I) (curve *2*) and the model compound (III) (curve *3*).[18]

It follows from the fluorescence quantum yields for the polyester (I) and the model (III) (~0.3) and for the polyester (II) (less than 0.1) that the probability of the fluorescence of the exciplex formed as a result of the interaction of the excited carbazolyl group of the model (III) with a terephthalate group is lower than for the carbazolyl group. Comparison of the fluorescence lifetimes of compounds (I), (II), and (III) justifies the hypothesis that the reduced fluorescence intensity of the carbazolyl groups of the polyester (II) is due to the dynamic quenching of the fluorescence by terephthalate groups.

A method has been proposed[21] for the synthesis of carbazole-containing polyurethanes involving the polycondensation of 9-(6-hydroxy-5-hydroxymethylhexyl)-carbazole with aliphatic di-isocyanates in boiling anisole:

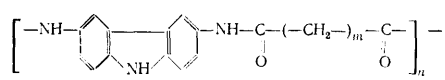


(IV)

$m = 2,6$.

The spectroscopic properties of the polymers (IV) and (I) are similar, i.e. are determined mainly by the carbazole chromophore without an admixture of exciplex states.

The polyamides (V), containing carbazole groups in the main chain and not in the side chain, have been obtained by the polycondensation of 3,6-diamino-9-ethylcarbazole with aliphatic dicarboxylic acid dichlorides in 9-ethylcarbazole using triethylamine as the catalyst:[22]



V

$m = 2, 6, 8$.

The fluorescent properties of the polymers (V) and of the model compound 9-ethyl-3,6-bis(propionylamino)carbazole have been investigated in solutions in hexane and *m*-cresol. It is shown that solutions of both compounds are characterised by the same monomeric fluorescence without a contribution due to the glow of excimers. The significant bathochromic shift of the fluorescence band, observed for the solution in *m*-cresol ($\lambda_{max} = 410$ nm) is explained by the authors by the formation of a hydrogen bond between the OH group of the solvent and the amide bond in the test substances.

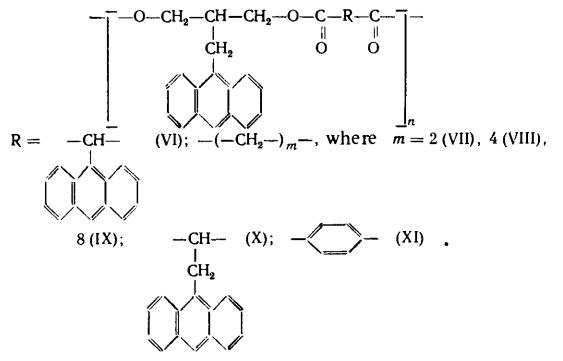
2. Anthracene-Containing Polymers

It is known[23] that anthracene-containing polymerisation systems of the type of poly-9-vinylanthracene belong to the class of photosemiconductors, which are promising for the preparation of electrophotographic layers. Presumably polycondensation polymers with anthracene fragments in the side chain will also be of interest as photoconducting materials. However, all the available literature data on such polymers deal primarily with questions of electronic energy transfer in these systems and with the observation of excimer glow and not with their photoconducting characteristics.

Among anthracene-containing polycondensation polymers, one should distinguish polyesters,[24-28] polyurethanes,[26-28] and polymeric quaternary ammonium salts (polyionenes).[29-31]

In order to obtain the polyesters (VI)–(XI), 2-(9-anthryl)-methylpropane-1,3-diol was subjected to polycondensation with dicarboxylic acid esters at 150–160 °C in the presence of catalytic amounts of calcium acetate and antimony trioxide:[24]

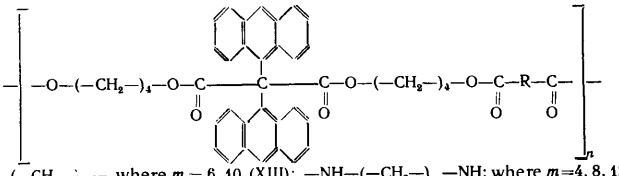
†Here and henceforth monomer fluorescence should be understood as the emission associated exclusively with the nature of the individual chromophoric polymer fragments, while the excimer and exciplex fluorescence should be understood as the emission by complexes consisting respectively of two identical or different molecules, one of which is in the ground state, while the other is in an excited state.



The polymers synthesised are soluble in tetrahydrofuran (THF) and, according to gel-permeation chromatographic data, have a low molecular weight (n = 2–7). The polyesters (VII), (IX), and (XI) were also synthesised by the reaction of the initial propanediol with the dithiol esters of the corresponding dicarboxylic acid at 150–160 °C for 2–3 h in an atmosphere of nitrogen and then *in vacuo* for 13–18 h in order to remove the thiophenol.[25] This method made it possible to obtain polyesters with higher molecular weights (n = 4–25).

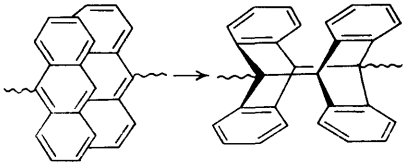
A study of the luminescence-spectroscopic properties of solutions and films of polymers as well as solutions of the model 1,3-diacetoxy-2-(9-anthryl)methylpropane (XII) showed that the light absorption properties of all the substances investigated are similar. The fluorescence spectra of solutions of the polymers contain both monomer bands with λ_{max} = 392, 415, and 440 mn as well as bands due to excimer glow with λ_{max} = 460 nm (Fig.2). It was found that the ratio I_e/I_m for the polymer solutions falls from 0.431 to 0.024 in the series of compounds (VI) > (X) > (VII) > (VIII) > (IX) > (XI). In the polymer films the excimer fluorescence predominates over the monomer fluorescence (Fig.2*b*). The fact that the polyester (VI) has the most intense excimer fluorescence is apparently associated with the high efficiency of the energy transfer in this polymer. A study of the dependence of I_e/I_m on the content of the polymer (VI) in solution showed that the interaction between the anthryl units predominates at a concentration $\leqslant 10^{-3}$ M (I_e/I_m = const.), while at higher concentrations the contribution of intermolecular interactions increases (I_e/I_m increases with increasing concentration). The occurrence of energy transfer process between various phosphor units has been demonstrated in relation to the polyester (X): on excitation of fluorescence with light having λ = 280 nm, which is absorbed by naphthyl groups, emission from the anthryl units alone was observed (Fig.2*b*).

A method has been proposed[26,27] for the synthesis of the polyester (XIII) and the polyesterurethanes (XIV) by the polycondensation of 9,10-bis-4-(hydroxybutylenoxycarbonyl)dianthracene with acid dichlorides or di-isocyanates:



The polymers obtained are readily soluble in chloroform and methylene chloride and have comparatively high molecular weights.

It has been shown[27] that, when the polymers (XIII) and (XIV) are irradiated with light at a wavelength of 300 nm at 196 K, a small fraction (up to 5%) of the dianthracene units are photolysed to anthroate groups:



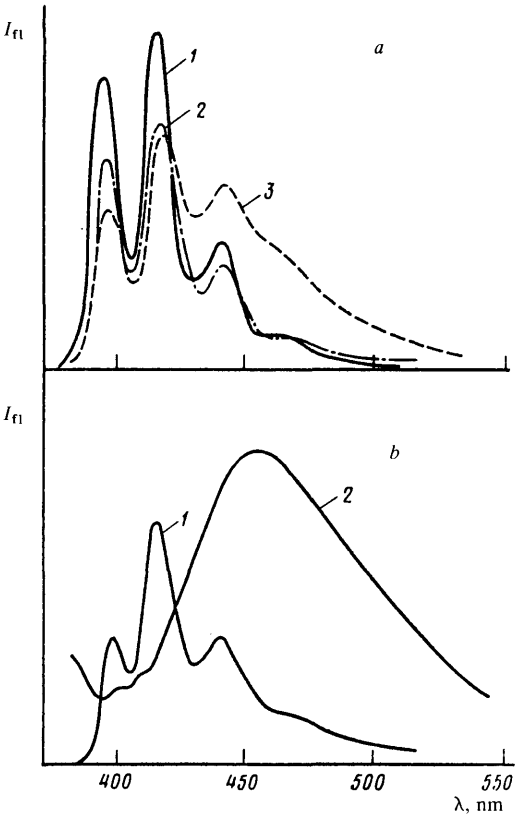
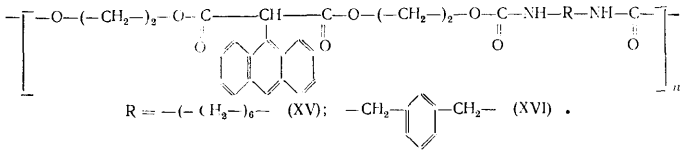


Figure 2. Fluorescence spectra: *a*) of solutions in THF of the model compound (XII) (curve *1*), the polyester (X) (curve *2*), and the polyester (VI) (curve *3*); *b*) of a solution of the polyester (VIII) in THF (curve *1*) and of a film of the polyester (VII) (curve *2*).[24]

The anthroate end groups are formed as sandwich dimers, which gradually decompose to the monomeric state on heating.[27] The formation of dimers is indicated by a broad structureless band with a maximum at 500 nm in the fluorescence spectra of the polymers after photolysis at 196 K. In the specimens of polyesterurethanes (XIV) the structure of the sandwich dimers is retained at 20 °C, while in the polyesters (XIII) these complexes are stable only at low temperatures. The fluorescence spectra of the isolated anthroate end groups show that the rotational mobility of

the phosphor units in the polymer (XIV) is lower than in (XIII). The restricted mobility of these groups influences the formation of new dianthracene units on irradiation with light at the wavelength corresponding to the ^1L_a absorption band of the anthroate group.

The anthracene-containing polyurethanes (XV) and (XVI) were obtained[28] by the interaction of bis(2-hydroxyethyl)-9-anthrylmethyl malonate and the corresponding di-isocyanates in anisole for 6 h:



The polymers (XV) and (XVI) are soluble in THF and have molecular weights ranging from 4100 to 11000 according to gel-permeation chromatographic data.

Fig.3 presents the absorption and emission spectra of polyurethane (XV) films. The broad absorption bands at 360 and 380 nm are apparently associated with the presence of sandwich dimers, which are formed as a result of the close spacing of the anthryl groups parallel to one another. The fluorescence spectra of solutions of the polymers (XV) and (XVI) in THF correspond to transitions involving the emission from both monomeric units and excimers. The fluorescence excitation spectra of the polymer films are broader than the analogous spectra of the solutions, which indicates an appreciable role of the interaction between the macromolecules in the solid specimen.

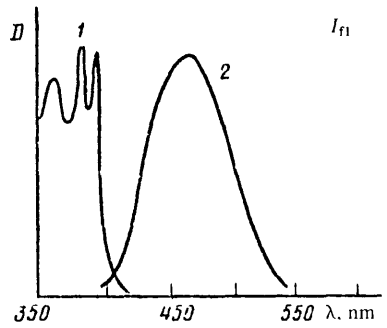
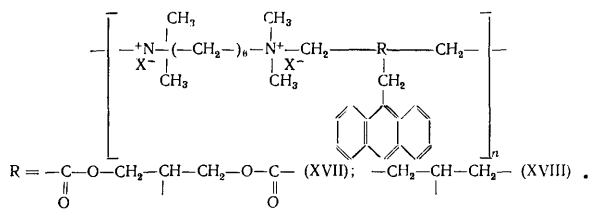


Figure 3. Absorption (curve *1*) and emission (curve *2*) spectra of a film of the polyurethane (XV).[28]

The light absorption and fluorescence properties of the polyionenes obtained by the Menshutkin reaction involving the interaction of 1,3-bis[halogenoacetoxy-2(9-anthryl)-methylpropane] or 2-[(9-anthryl)methyl]trimethylene halides with tertiary diamines have been described in a series of communications:[29-31]



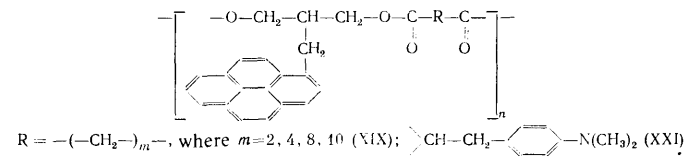
The polymers (XVII) and (XVIII) were synthesised in dimethylformamide, dimethylacetamide, dimethyl sulphoxide, or sulpholan at 40–60 °C over periods of 20–126 h.

Like other polymers with a similar structure,[15] the polyionenes obtained are apparently capable of forming conducting radical-ion salts with powerful electron acceptors (of the type of tetracyanoquinodimethane). The presence of the electron-donating anthryl groups in the polymers should have a favourable effect on the electrophysical characteristics of these systems.

The study of the fluorescent properties of the polyionenes (XVII) and (XVIII) showed that the formation of hydrophobic domains in aqueous solutions due to the anthrylmethyl groups, which are responsible for the appearance of a broad structureless excimer emission band with a maximum at 500 nm, is characteristic of these substances. The addition of methanol to solutions of the polymers promotes the decomposition of the hydrophobic domains and diminishes the intensity of the excimer fluorescence. On the other hand, the addition of electrolytes intensifies the excimer glow and this effect is greater the higher the ionic strength of the solution.

3. Pyrene-Containing and Other Polycondensation Polymers

Tazuke and co-workers considered the synthesis of a series of pyrene-containing polyesters based on monomers of the type of 3-pyrenylpropane-1,3-diol.[25,32-35] The use for this purpose of the reaction of the diol with dithiol esters of dicarboxylic acids at 150–170 °C initially in an inert atmosphere and then *in vacuo* made it possible to obtain the polymers (XIX) with molecular weights higher by a factor of 2–5 than in the traditional polycondensation of diols with acid dichlorides:[25,35]



The light absorption properties of the polyesters (XIX) are independent of the nature of the acid residue and are similar to the properties of the model compound (XX)—the product of the acylation of 3-pyrenylpropane-1,3-diol (λ_{max} = 344 nm). On the other hand, in the fluorescent properties of these systems there are differences (Fig.4) associated with the appearance of the exciplex glow (λ_{max} = 480–490 nm) in the case of the polymer.

The emission spectra of the polymers (XIX) are close to those of other pyrene-containing polyesters (XXI) with dimethylaniline side groups.[32-34] The latter were synthesised by the bulk polycondensation of the corresponding propanediol with diethyl 4-(*NN*-dimethylamino)benzyl malonate in the presence of calcium acetate as the catalyst at 160–210 °C *in vacuo*.

Polymers similar to the polyester (XXI) and containing electron-donating (*NN*-dimethylaniline) and electron-accepting (pyrenyl) groups are of interest from the standpoint of the formation of charge-transfer complexes, which as a rule exhibit an enhanced photosensitivity over a wide spectral range.[15,23]

The absorption and fluorescence spectra of solutions of the model compound (XX) and of the polyester (XXI) are compared in Fig.4*b*. Comparison of the absorption spectra of the polymer and the model indicates a weak interaction between the chromophores in the ground state. It was

found[32] that the ratio of the intensities of the exciplex fluorescence with λ_{max} = 498 nm and of the monomer fluorescence with λ_{max} = 377 nm increases with increasing concentration of the polymer solution and the character of the relation is determined by the nature of the solvent. Whereas in an effective solvent (dichloroethane) the relation $I_e/I_m = f(c)$ is linear, in a poor solvent (mesitylene) it tends to saturation. The authors concluded[32] that in mesitylene the intermolecular formation of the exciplexes reaches saturation at an early stage, while in dichloroethane their formation is facilitated by "allosteric" association in which the macromolecules are arranged relative to one another in such a way that the electron-accepting fragments of one of them adjoin the electron-donating fragments of another without disturbing the conformation of the polymer as a whole. Association of this kind is particularly favourable for macromolecules with a moderate molecular weight. Indeed the $I_e/I_m = f(n)$ relation for the polyesters (XXI), in which the degree of polycondensation n is controlled and varies from 1 to 18, passes through a maximum at n = 14 (in dichloroethane) and n = 7 (in mesitylene).[33]

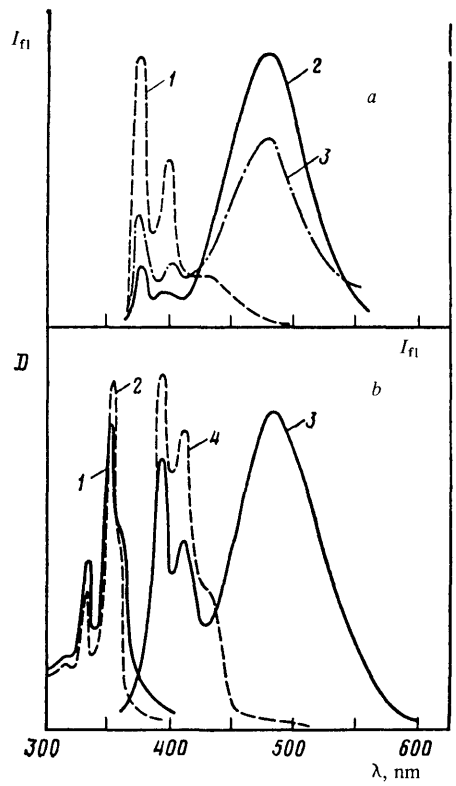
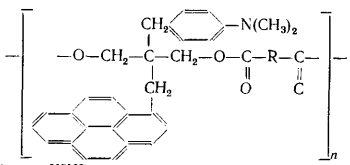


Figure 4. *a*) Emission spectra of solutions in THF of the model compound (XX) (curve *1*) and the polymer (XIX) with R = $-(CH_2)_2-$ (curve *2*) and $-(CH_2)_{10}-$ (curve *3*); *b*) absorption spectra (curves *1* and *2*) of solutions in 1,2-dichloroethane and emission spectra (curves *3* and *4*) of solutions in dioxan of the model compound (XX) (curves *2* and *4*) and the polymer (XXI) (curves *1* and *3*).[32]

Together with intermolecular complex formation, intramolecular association also makes some contribution to the formation of exciplexes. This has been confirmed by the observation[33] that the model compound containing both the dimethylaniline and pyrenyl fragments exhibits an appreciable exciplex fluorescence regardless of the concentration of the solution. On the other hand, a solution of a mixture of two model compounds, each of which contains one of the above groups, does not exhibit an exciplex glow.

It has been shown[34] that the role of the intramolecular interactions in the polyesters (XXI) becomes dominant when the temperature is reduced to 77 K. In this case the band with λ_{max} = 498 nm disappears from the fluorescence spectra of the polymers and a new band appears with λ_{max} = 440 nm, which has been attributed to the emission of an electron donor–electron acceptor complex. Its formation is confirmed by the broadening of the band in the absorption spectra of solutions of the polymer (XXI) relative to the spectra of the model compounds. In contrast to the glow of the exciplexes, the intensity of the fluorescence of the donor–acceptor complexes increases with increasing molecular weight of the polymer and with decrease of temperature and is almost independent of the polymer concentration in solution.

The polyesters (XXII), which also contain the pyrene and dimethylaniline groups, but, in contrast to the polymers (XXI), these are attached to a single carbon atom, have been investigated:[35]



R = $-(-CH_2-)_m-$ (XXII); $-NH-(-CH_2-)_m-NH-$ (XXIV), where m=2–10.

Measurement of the fluorescence spectra of the polyesters (XXII) and of the model compound (XXIII)—the acylated 2-(4-*NN*-dimethylaminobenzyl)-2-(1-pyrenylmethyl)propane-1,3-diol—in solution in THF demonstrated the presence of a weak band with λ_{max} = 380 nm in the region corresponding to emission from the monomeric pyrene units and of intense exciplex fluorescence with λ_{max} = 520 nm.

Comparison of the emission spectroscopic data for the polymers (XXI) and (XXII) shows that the mutual approach of the electron-donating and electron-accepting fragments entails a bathochromic shift of the exciplex fluorescence. The authors emphasise[35] that the exciplex bands in the fluorescence spectra of solutions of the polyesters (XXII) and the model compound (XXIII) have different forms. The difference is apparently caused by the fact that only the intramolecular interaction of the donor with the acceptor occurs in solutions of the model compound at a concentration less than 10^{-5} M, while in the case of polymers both intramolecular and intermolecular interactions take place.

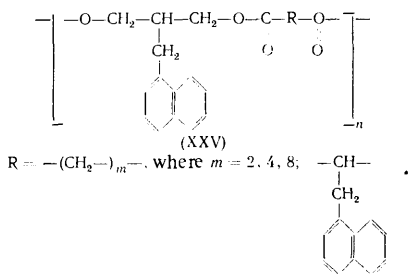
Other polymers with pyrenyl and dimethylaniline groups, namely the polyurethanes (XXIV), have been described.[36] They were synthesised by the interaction of 2-(4-*NN*-dimethylaminobenzyl)-2-(1-pyrenylmethyl)propane-1,3-diol with di-isocyanates in anisole at 150–160 °C in the presence of triethylamine as the catalyst.

The study of the fluorescence characteristic of solutions of the polymers (XXIV) showed that the position of the exciplex fluorescence maximum is in the range from 485 to 505 nm and depends significantly on the molecular weight of the polymer and its concentration in solution. The ratio I_e/I_m increases with increasing concentration in the intermediate range of molecular weights, which indicates the association of the macromolecules in solution. Comparison of the spectra of polymers in which the number of methylene

groups in the di-isocyanate residue is 6 and 8 demonstrated convincingly that even small changes in the structure of the polymers (XXIV) and hence in the rigidity of the polymer chain have an appreciable influence on the intermolecular and intramolecular formation of exciplexes and the fluorescence properties of the polymer.

Apart from the polymeric system with pyrenyl fragments examined above, polycondensation polymers with phosphor units of the naphthalene,[37-40] *p*-phenylenediacrylic,[41,42] 3-methoxybenzanthrone,[43] and naphthalimide[44] types are known.

Polyesters with the naphthylmethyl side groups (XXV) have been synthesised by the polycondensation of 2-[(1-naphthyl)-methyl]propane-1,3-diol with the diethyl esters of dicarboxylic acids at 150–160 °C for 3 h in an inert atmosphere and then *in vacuo* for 10 h:[37]



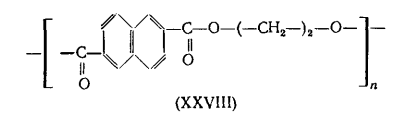
(XXV)

R = $-(CH_2-)_m-$, where $m = 2, 4, 8$; $-CH-$ with CH_2 and a naphthyl group

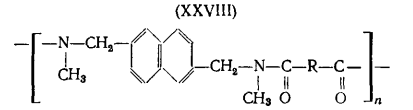
According to gel-permeation chromatographic data, the polymers have a low molecular weight (n = 3–10).

The study of the fluorescence properties of the polymers (XXV) was preceded by the investigation of model compounds—1,3-bisacetoxy-2-(1-naphthyl)methylpropane (XXVI) and di[3-(1-naphthyl)propyl]adipate (XXVII). It was found that, in contrast to the emission spectra of the model compound (XXVI), those of solutions of the polymers (XXV) contain, together with the monomeric fluorescence band having λ_{max} = 324 nm, also a broad excimer band with λ_{max} = 400 nm. The intramolecular formation of excimers takes place even in those cases where the naphthyl groups are separated by 16 carbon atoms and two oxygen atoms. The ratio I_e/I_m for the polymeric system (XXV) is higher that for the corresponding dimeric system (XXVII). The authors[37] explain this by the fact that the local concentration of the naphthyl units in the ground state in the vicinity of the excited group, considered in isolation, is higher in the polymer macromolecule than in the dimeric system.

The fluorescence properties of naphthalene-containing polymers of another type, namely the polyesters (XXVIII) and polyamides (XXIX) with naphthalene nuclei bound directly in the main polymer chain, have been described:[38,39]



(XXVIII)



(XXIX)

R = $-(-CH_2-)_m-$, where $m = 2, 4, 6, 8$.

Comparison of the fluorescence properties of the polyesters (XXV) and (XXVIII) shows that the introduction of the naphthalene fragments into the main polymer chain induces a bathochromic shift of the monomer and excimer glow. The ratio of the intensities of the excimer (λ_{max} = 420 nm) and monomer (λ_{max} = 370 and 385 nm) fluorescence of solutions of the polymer (XXVIII) in chloroform increases by a factor of 3 when its concentration rises from 0.024 to 43 dl g^{-1} and, on passing to solid films, the increase is by a factor greater than 6 (compared with the minimum concentration in solution). The same type of dependence of I_e/I_m on the polymer concentration in solution has been observed also for the phenyl-containing polyester.[39] However, in the case of the polyester (XXVIII) one observed the formation of intramolecular excimers, which fluoresce even in very dilute solutions, and this is apparently associated with the longer lifetime of the excited states of the naphthyl chromophores. This is valid also for other types of naphthalene-containing polymers.[1]

We shall consider the formation of fluorescent intermolecular charge-transfer complexes in relation to the polyamide (XXIX).[38] We may note that the only complete review of studies on such complexes has been published recently.[40]

Fig.5 presents the fluorescence spectra of dilute solutions of the polyamide (XXIX) (m = 4) in methylene chloride in the presence and absence of a low-molecular weight electron donor (triethylamine). Evidently, when triethylamine is added to the polyamide, the intensity of the intrinsic fluorescence of the polymer, with a maximum at 360 nm, diminishes and a broad exciplex fluorescence band appears with a maximum at 500 nm. A linear relation has been found between the concentration of triethylamine and the ratio I_e/I_m. It has been shown that tendency towards the formation of exciplexes diminishes in the series of polyamides with decrease of m in the acid residue, i.e. in parallel with increasing steric restriction of the mobility of the naphthyl groups.

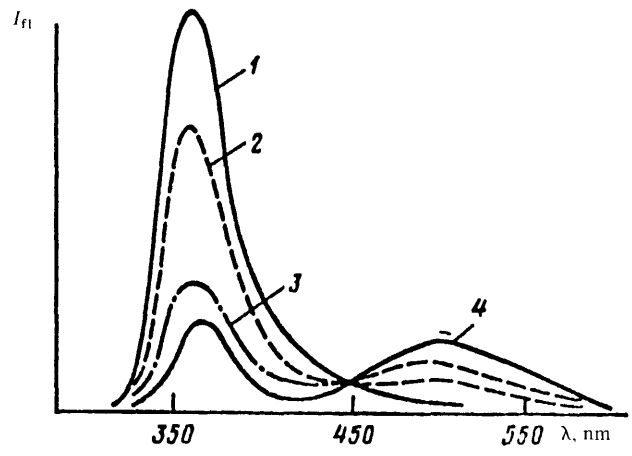
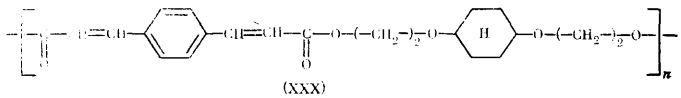


Figure 5. Fluorescence spectra of solutions of the polyamide (XXIX) (m = 4) in methylene chloride in the absence of triethylamine (curve *1*) and in the presence of various concentrations of triethylamine (M): *2*) 0.01; *3*) 0.06; *4*) 0.19.[38]

An industrial photoconducting polymer (XXX), used for the preparation of printing plates and obtained from *p*-phenylenediacrylic acid and 1,4-bis(2-hydroxyethoxy)-cyclohexane, has been investigated from the standpoint of its fluorescence properties:[41,42]



(XXX)

At the same time a study was made of the fluorescence characteristics of the model compound (XXXI), namely the diethyl ester of *p*-phenylenediacrylic acid. Fig.6, which presents the emission spectra of these two systems, shows that those of solutions of the model compound and the polymer (XXX) contain short-wavelength monomer fluorescence bands with a maximum at 370 nm and a longer-wavelength broad band due to the excimer glow, the intensity ratio of these bands depending on the concentration of the solution. The spectrum of a film of the polymer shows only the excimer fluorescence with a maximum at 470 nm.

It has been shown[41] that the kinetics of the decay of the glow in the region of 470 nm can be fitted by the sum of two exponential functions; the short-lived fluorescence is due to the monomer, but the long-lived fluorescence is due to the excimers. The lifetime of the long-lived fluorescence diminishes with increasing concentration of the phenylene diacrylate groups, which indicates a bimolecular character of the decay of the excimer glow. It has been found that the excimers are formed on excitation of pairs of chromophores already present in solution before excitation.

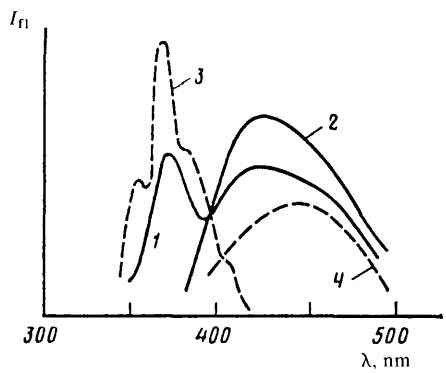


Figure 6. Emission spectra of dilute solutions of the polymer (XXX) (curve *1*) and the model compound (XXXI) (curve 3) in 1,2-dichloroethane, of a film of the polymer (XXX) (curve *2*), and of a concentrated solution of the polymer (XXXI) (curve *4*).[41]

The melaminotoluene-*p*-sulphonamideformaldehyde (MTSF) resins, which are frequently used as the polymer base for the preparation of daylight fluorescent pigments,[4] can be classified as an aliphatic polycondensation polymer. The phosphor containing a reactive group is added in the synthesis stage of the MTSF resins, which consists in heating a mixture of toluene-*p*-sulphonamide, melamine, and formaldehyde; the resulting polymer is chemically bound to the phosphor molecule. The chloromethyl, hydroxymethyl, carboxy, anhydride, or amino-groups can be used as the reactive groups of this kind, while 3-methoxybenzanthrone residues[43] and derivatives of 1,8-naphthalic acid[4,44] can serve as the phosphor fragments.

Analysis of the available data on the synthesis and spectroscopic properties of fluorescent polycondensation polymers permits the conclusion that those whose phosphor fragments were introduced into the macromolecule via the diamine (diol) component and not via the acid component have been most thoroughly investigated. The phosphor groups are mainly responsible for the long-wavelength absorption and fluorescence characteristics of the polymers and the emission spectra can show both the monomer bands and the excimer (exciplex) fluorescent bands. The tendency towards the formation of exciplexes increases appreciably when the macromolecule contains fragments capable of intramolecular and intermolecular donor–acceptor interaction.

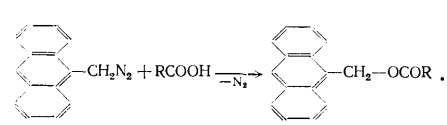
III. PRODUCTS OF POLYMER-ANALOGUE TRANSFORMATIONS

The first fluorescent polymers obtained by the method of polymer-analogue transformations have been proteins coloured by active luminescent dyes. A condition for the covalent binding of these dyes to proteins having SH, OH, and H_2N side groups is the presence in them of reactive groups of the type of SO_2Cl, N=C=O, and N=C=S. Derivatives of naphthalene, anthracene, fluorescein, rhodamine, and a number of others are used to dye proteins.[45]

The study of protein macromolecules labelled with luminescent dyes makes it possible to investigate the properties of electronically excited states and the specific features of the electronic transitions in such systems and enables one to follow the kinetics of the structural and physicochemical transformations of proteins.[46] Furthermore, the purely analytical use of the luminescence for the determination of the protein in biological preparations is of considerable interest.[4]

Some of the early investigations of macromolecules with phosphor side groups were those of Wahl,[47,48] who described the interaction of polymers containing amino-groups (of the type of polyvinylamine, poly-*p*-aminostyrene, and polyethyleneimine) with 1-dimethylaminonaphthalenesulphonyl chloride. The reaction was carried out by mixing an aqueous solution of the polymer with a solution of the sulphonyl chloride in acetone. Depending on the reactant ratio, fluorescent polymers with different numbers of naphthalene groups in the side chain are formed.

Later the luminescent units were introduced into the side chains of polymers by the reaction of their carboxy-groups[49–53,55] (see also Metaga and Kubota[54]), the acid chloride groups,[56] hydroxy-groups,[57–61] or benzene rings.[51,62] The interaction of polymeric acids of the type of polyacrylic and polymethacrylic acids or their copolymers with phosphors such as 9-anthryldiazomethane, 9-methyl-10-anthryldiazomethane, or diazomethyl α-naphthyl ketone has been investigated.[49–51] The reaction was carried out both in a homogeneous medium (methanol) and in immiscible solvents (water–hexane) at 20–55 °C:

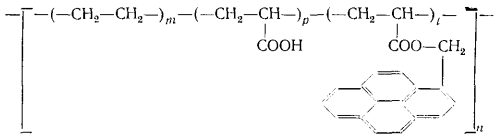


The concentration of the fluorescent groups introduced can be varied within wide limits by altering the polymer : diazomethane ratio. The fluorescence properties of the resulting polymers were similar to those of the model 9-anthrylacetoxymethane. Monomer fluorescence without an admixture

of the glow due to excimers is characteristic of both types of compounds. The study of polymers labelled with anthracene fragments made it possible to employ the method of polarised luminescence[63,64] for the investigation of the relaxation phenomena in solutions of macromolecules (intramolecular and intermolecular interactions, structure formation, gel formation, etc.).

The interaction between 9-anthryldiazomethane and the copolymers of styrene with acrylic, methacrylic, and vinylbenzoic acids followed by spectrophotometric measurements on the reaction product in the range 390–410 nm has been suggested for the analytical determination of the content of carboxy-groups in these polymers.[50]

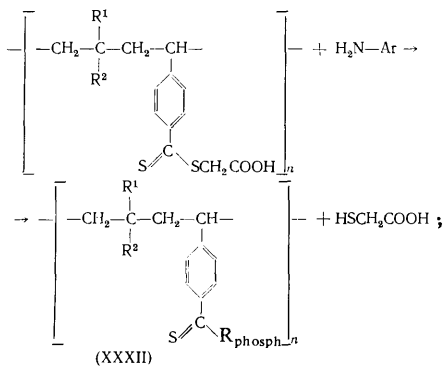
Polymeric styrene-containing sensitisers (XXXI), which are of interest for the preparation of photosensitive layers, have been obtained[53] from a radiation-modified polyethylene containing 45–47% of grafted COOH groups. Compound (XXXI) was synthesised by the reaction of the modified polyethylene with 1-hydroxymethylpyrene in THF or acetonitrile at 60 °C in the presence of dicyclohexylcarbodiimide as the catalyst.



(XXXI)

The study of the fluorescence properties of films of the polymers (XXXI) with different degrees of esterification showed that the intensity of the excimer fluorescence with λ_{max} = 465 nm increases as the concentration of the pyrene groups rises.

A number of interesting coloured polymers exhibiting a weak fluorescence have been described.[52] They were obtained by the reaction of polyethylene-4-thiobenzoylthio-2-acetic acid or the copolymers of the initial thioester with styrene, methyl methacrylate, or methacrylic acid and diamines of the type of Acridine Yellow, 1-aminoanthraquinone, and Cresol Blue:



(XXXII)

$R^1 = C_6H_5$, $R^2 = H$; $R^1 = CH_3$, $R^2 = COOH$ or $COOCH_3$; R_{phosph} = phosphor residue.

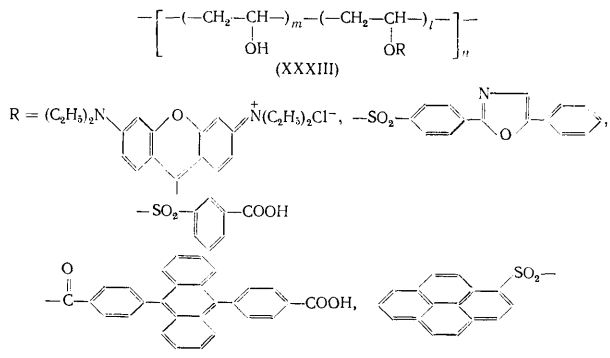
The reaction is carried out in a 1 : 1 dimethylformamide–benzene mixture with a polymer : amine ratio of 2 : 1 for 24 h at room temperature. The fluorescence properties of the copolymers (XXXII) were not investigated in detail. It was only noted that the intensity of the glow of the initial dyes, for example, of Acridine Yellow, diminishes appreciably after binding to the polymer. The authors[52] do not give any explanation of the observed phenomenon. In our view its possible cause is the formation of hydrogen bonds between the diaminoacridine fragment and the hydrogen donor present in the system, namely thioglycolic acid, which promotes the quenching of the fluorescence according to Mataga and Kubota.[54]

Whereas the carboxy-groups of the polymers have been used in a number of studies[49–53] to form strong covalent bonds with the fluorescent molecule, in the systems described by Fenyo[55] the bond linking polyacrylic and polymethacrylic acids to the phosphor amine is salt like. Fenyo's aim[55] was to investigate the conformational behaviour of the macromolecule in solution. Compounds which the authors chose as the amines were auramine, which does not dimerise and exhibits a weak fluorescence, and 9-aminoacridine hydrochloride, which is capable of forming dimers and exhibits an intense fluorescence. It has been shown that the binding of the dye is determined by three factors: the nature and conformational state of the polyions (the degree of ionisation α), the polymer : dye molar ratio, and the ionic strength of the solution. The intensity of the emission by auramine increases by a factor of 100 in the presence of poly(methacrylic acids). An increase of the fluorescence quantum yield and of the relative content of the bound dye with increasing polymer : dye ratio has been observed for this compound.

An increase in the degree of ionisation of the polymeric acid diminishes the efficiency of the binding of the dye to the polymer in the case of auramine and, conversely, leads to its increase in the case of 9-aminoacridine hydrochloride. Furthermore, it has been observed that, for low values of α, the addition of poly(methacrylic acids) to the last phosphor diminishes the intensity of its fluorescence. Fenyo[55] put forward an explanation of the observed differences in the behaviour of the phosphors on the basis of a comparison of the rigidities of the skeletons of their molecules and the presence of side groups in the latter.

We shall now proceed to the polymer-analogue transformations of hydroxylated polymers. Fluorescein isothiocyanate has been used[57] as reagent with the OH groups of a constituent of starch, namely amylose having a molecular weight of 1700. The fluorescence lifetimes of the resulting polymer were measured at different concentrations and pH of the solutions.

The luminescence-spectroscopic properties of films and solutions of poly(vinyl alcohol) (XXXIII), containing four types of phosphors as side groups, namely diphenyloxadiazole, diphenylanthracene, rhodamine B, and pyrene, have been investigated:[58–60]



(XXXIII)

The polymers (XXXIII) were synthesised by treating poly(vinyl alcohol) with the corresponding sulphonyl chloride or acid chloride in *N*-methylpyrrolidinone, initially at room temperature and then at 60–70 °C. Depending on the ratio of the initial reactants, polymers containing from 5 to 10 phosphor fragments per 1000 elementary units were obtained.

The polymers (XXXIII) exhibit an intense fluorescence and are highly soluble in water, which permits their use as luminescent probes in the study of biological membranes.[63] The polymeric structure of these probes determines their enhanced selectivity in relation to individual cell components as compared with low-molecular-weight phosphors.

Fig.7 presents the absorption and emission spectra of specimens of the first three types of polymers (XXXIII) in the form of thin films. Their comparison with the spectra of the initial phosphor monomers[4] demonstrates their similarity. The similarity of the fluorescence characteristics of the polymers to those of the corresponding low-molecular-weight compounds confirms the monomer character of the emission without an appreciable contribution by excimer states. The same conclusion can be reached on the basis of a comparison of the emission spectra of solutions of these systems.

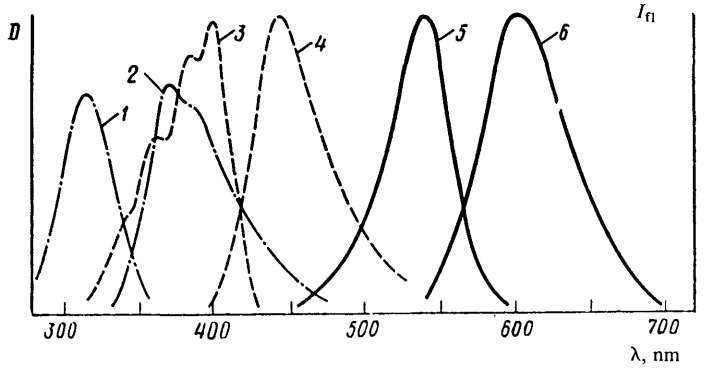
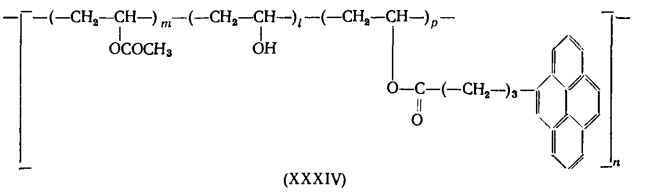


Figure 7. Absorption (curves *1*, *3*, and *5*) and fluorescence (curves *2*, *4*, and *6*) spectra of films of the polymers (XXXIII) containing diphenyloxazole (curves *1* and *2*) diphenylanthracene (curves *3* and *4*), and rhodamine B (curves *5* and *6*) units in the side chain.[60]

The fluorescence spectra of the pyrene-containing polymers (XXXIII) are more complex (Fig.8). Evidently, depending on the concentration of the solution, either only monomer fluorescence bands due to the pyrene groups with λ_{max} = 376, 395, and 415 nm are present in the spectra or they are accompanied by the excimer band with λ_{max} = 495 nm. The authors[59,60] observed a direct linear relation between the ratio I_e/I_m and the concentration of an aqueous solution of the polymer (XXXIII). When water was replaced by a more viscous solvent (ethylene glycol) a sharp decrease of the intensity of the excimer glow was observed, while the intensity of the monomer fluorescence bands was unchanged. Evidently the increased viscosity of the solvent diminishes the rate constant for the intramolecular formation of excimers, which agrees with a diffusion-controlled mechanism.

The latter conclusion has also been confirmed by the results of Cuniberti and Perico,[61] who investigated a partly hydrolysed poly(vinyl acetate) (XXXIV) treated with 4-(3-pyrenyl)butyric acid in THF in the presence of trifluoroacetic anhydride at 50 °C. This method made it possible to obtain a polymer with an average spacing between the pyrenyl groups equivalent to approximately 200 units:



It follows from the fluorescence spectra of solutions of the polymer (XXXIV) in methanol and ethylene glycol that both a monomer emission with λ_{max} = 396 nm and an excimer emission with λ_{max} = 480 nm are observed in the former solvent. In the more viscous ethylene glycol the excimer fluorescence is absent. A dependence of the ratio I_e/I_m on the viscosity of the medium has been observed for mixtures of solvents of similar types.[61]

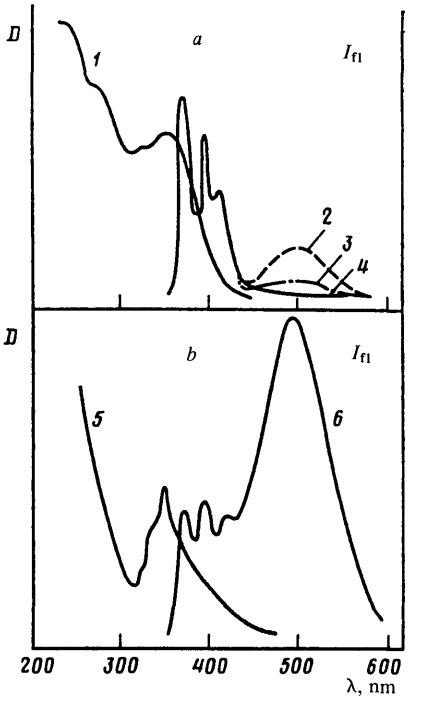
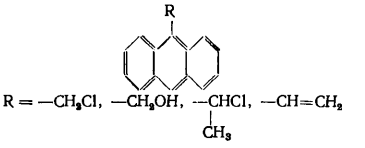


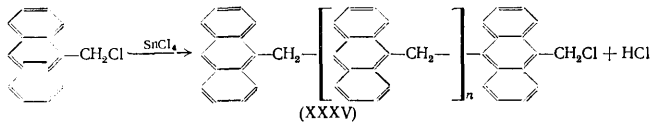
Figure 8. Absorption (curves *1* and *5*) and fluorescence (curves *2*, *3*, *4*, and *6*) spectra: *a*) of aqueous solutions of the pyrene-containing polymer (XXXIII) at concentrations of 0.28 M (curve *2*), 0.14 M (curve *3*), and 0.017 M (curves *1* and *4*); *b*) of a film of the polymer (XXXIII) (curves *5* and *6*).[60]

The Friedel–Crafts reaction of anthracene derivatives with the benzene rings of the macromolecules proved to be a fairly convenient method of synthesis of fluorescent polymers by polymer-analogue transformation.[51,62] It has been suggested that derivatives of the type



be used as the anthracene compounds. Their reaction with phenyl-containing polymers of the polystyrene, poly-α-methylstyrene, poly(benzyl vinyl ether), or poly(benzyl propenyl ether) was carried out at room temperature or at −78 °C for 0.5–360 h using $SnCl_4$ or boron trifluoride as the catalysts.[62] The polymers formed contain from 0.2 to 83 anthracene groups per 1000 polymer units and possess fluorescence properties close to those of the model benzylanthracene (the bands in the fluorescence spectrum of a solution in toluene at λ_{max} = 395, 425, and 440 nm).

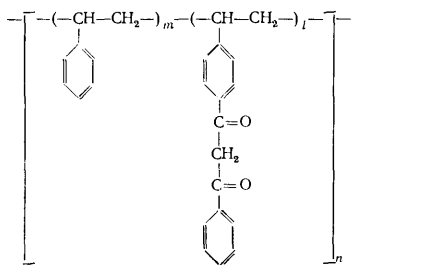
It was shown[62] that polycondensation processes occur simultaneously with alkylation under the conditions of the Friedel–Crafts reaction:



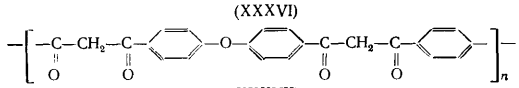
(XXXV)

Thus in the absence of the phenyl-containing polymer, the homopolycondensation of 9-chloromethylanthracene gives rise to the polymer (XXXV) MW = 1500) in 85% yield, the fluorescence spectrum of its solution in toluene containing a short-wavelength band at λ_{max} = 420 nm and a long-wavelength band at λ_{max} = 445 nm, which slowly descends to 560 nm. Homopolycondensation reduces the yield of the alkylation reaction and can lead to the addition of groups of the type of (XXXV) to the phenyl-containing polymer, which is reflected in the fluorescence spectra.

Extremely interesting fluorescent polymers, the method of synthesis of which can also be regarded as approximately polymer-analogue transformations, have been described.[65] These compounds are chelate europium complexes of macromolecules containing β-diketone units as ligands: poly-*p*-benzoylstyrene (XXXVI) and polyaryl-β-diketone (XXXVII):



(XXXVI)



(XXXVII)

The polymers (XXXVI) were synthesised by the reaction of partly acetylated styrene with methyl benzoate in the presence of sodium amide in THF at 50 °C. The europium(III) complexes were obtained by mixing 1–2% solutions of the polymers in THF with a solution of europium trichloride in a THF–methanol mixture.

The interest in the polymeric complexes of the lanthanides is associated primarily with their intense monochromatic fluorescence. This property makes it possible to employ such complexes as the active media in laser technology, their operating characteristics being in a number of instances superior to those of traditional materials for analogous purposes.[5]

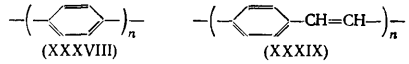
The chelate complexes of the polymers (XXXVI) and (XXXVII) are thermally stable but begin to decompose at 350 °C. The structure of the chelates has been investigated by infrared spectroscopy. It has been noted that the infrared spectrum of the polymer (XXXVII) has in the main an enolic structure with a broad absorption band in the region of 1350–1600 cm^{-1}.[65] When a chelate ring with Eu^{3+} is formed, a new intense band, corresponding to the asymmetric and symmetric vibrations of the C=O bonds and having a resonance structure appears in the spectrum at 1400–1530 cm^{-1}. The Eu^{3+} ions involved in complexes with the polymers (XXXVI) and (XXXVII) undergo radiative deactivation on excitation with light in the range of frequencies characteristic of inorganic crystals. The fluorescence spectra of the complexes contain two bands: one with a maximum at 613 nm, due to the $^5D_0 \rightarrow {}^7F_2$ transition, and the other, low-intensity band with a maximum at 580 nm, associated with the forbidden transition $^5D_0 \rightarrow {}^7F_0$. The intensity of the first fluorescence band of the complexes derived from the polymer (XXXVI) increases linearly with increase of the Eu^{3+} concentration to 3 wt.% and then remains constant. These complexes exhibit a fluorescence which is 20–30 times more intense that that of the complexes with the polymer (XXXVII) (containing 1% of Eu^{3+}). The authors[65] believe that this is due to the fact that, when the β-diketone groups are incorporated in the polymer chain, the formation of complex coordinate bonds between the Eu atoms and the β-diketone may be hindered by steric restrictions and by the decrease in the number of rotational degrees of freedom.

Since the fluorescent macromolecules arising in polymer-analogue transformations are in most cases polymers obtained by polymerisation methods, the rules governing their luminescence-spectroscopic properties are those noted in a review.[1] In the case of polymers the processes involving the transfer and migration of energy from the sites where it is absorbed to the sections of the macromolecule where the proximity and parallel arrangement of the planes of the chromophoric fragments promote the formation of excimers take place more or less effectively. A consequence of these processes is the presence in the fluorescence spectra of the polymers, together with the monomer emission band whose position and character are determined primarily by the nature of the chromophore, also of one or several excimer emission bands. In those cases where the absence of excimer emission may be regarded as proved, there is a great likelihood that no electronic excitation energy migration takes place along the polymer chain. One of the possible causes of the low capacity of such polymers for the formation of excimers is the increased flexibility of the macrochains, which disturbs the required planarity in the arrangement of the chromophores.

IV. AROMATIC FLUORESCENT POLYMERS

1. Carbochain Polymers

Aromatic carbochain polymers have been thoroughly investigated from the standpoint of light absorption properties, but their fluorescent characteristics have been investigated to a much lesser extent. An empirical rule established for linear polyenes and poly-*p*-phenylenes[66] (XXXVIII) is valid also for poly-*p*-xylidenes (XXXIX):[67]



(XXXVIII) (XXXIX)

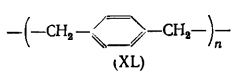
It states that, with increase in the length of the conjugated chain, the energy of the light quantum required for the excitation of the π-electron system diminishes and a bathochromic shift of the long-wavelength absorption band is

observed; after the chain has attained a specific length, the bathochromic shift ceases.[68,69] This shows that the fragment of the macromolecule which behaves as the chromophoric group is consistent with the model in which the number of conjugated π-bonds is less than the number equivalent to the length of the polymer chain. The chromophoric group of the polymer (XXXIX) is approximately equivalent to 3–4 elementary units of the macromolecule.[67]

The fluorescence properties of the polymers (XXXVIII) and (XXXIX) have been investigated.[70,71] A bathochromic shift of the fluorescence band has been observed for the poly-*p*-phenylene (XXXVIII) as its concentration in solution increases, without an appreciable change in the form of the absorption spectra,[70] which is associated with the major role of the energy transfer processes, whose intensity grows as the concentration of the solution rises. At concentrations above 10^{-3} M the energy transfer becomes so effective that quenching of the fluorescence is observed. The study of the effect of quenching agents such as tetracyanoethylene, chloranil, trinitrobenzene, dimethylamine, aminostyrene, and triethylamine on the luminescence of solutions of poly-*p*-phenylene (XXXVIII) showed that, when the absorption spectrum of the quenching agent overlaps the emission spectrum of the polymer, the quenching of the fluorescence can be accounted for by the Forster dipole–dipole energy transfer mechanism. This phenomenon occurs when chloranil is used as the quenching agent. On the other hand, when the absorption spectrum of the quenching agent and the emission spectrum with the polymer do not overlap, then the quenching takes place via a mechanism involving the migration of energy over a short distance or via the formation of donor–acceptor complexes. The latter occurs when aminostyrene, dimethylamine, or triethylamine are used as the quenching agents.

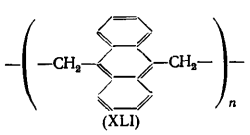
The study of the electronic absorption and emission spectra of polyphenylenes permits a detailed analysis of the mechanism of photoconduction in these polymers.[72]

The light absorption and luminescence properties of polymers with one or two methylene groups between the aromatic rings have been studied.[73–77] The electronic absorption spectra of poly-*p*-xylylene (XL) are characterised by a low-intensity band in the range 260–280 nm:[73,74]



(XL)

The phosphor-containing polymers of the type of poly-9,10-dimethyleneanthracene (XLI), obtained by the pyrolysis of 9,10-dichloromethylanthracene via the stage involving the formation of 9,10-anthraquinodimethane as an intermediate, are of more interest from the standpoint of optical properties:[75]



(XLI)

Fig.9 presents the absorption spectra of the initial 9,10-dichloromethylanthracene at 20 °C, of 9,10-anthraquinodimethane at −196 °C, and of the polymer (XLI) at 20 °C. Evidently the bands in the range 330–420 nm, which are characteristic of the anthracene nucleus, vanish almost completely on passing from 9,10-dichloromethylanthracene to 9,10-anthraquinodimethane. The spectrum of the latter contains only an intense band in the range 270–290 nm associated with the absorption by the anthraquinodimethane chromophore. As this compound is heated from −196 °C to room temperature, the intense absorption band at 291 nm disappears and a band with a maximum at 260 nm as well as a series of bands in the range 330–430 nm appear, confirming the structure of the polymer (XLI) formed.

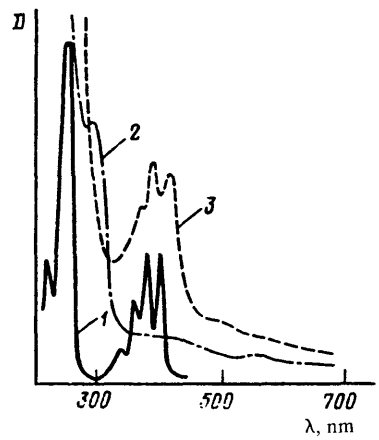


Figure 9. Absorption spectra of a solution of 9,10-dichloromethylanthracene in n-heptane at 20 °C (curve *1*), of 9,10-anthraquinodimethane deposited on a support at −196 °C (curve *2*), and of the polymer (XLI) on a support at 20 °C (curve 3).[75]

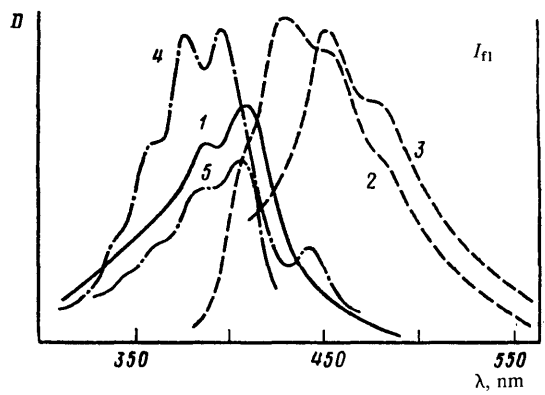


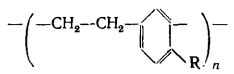
Figure 10. Electronic spectra of a solution of the polymer (XLI) in dimethylformamide: *1*) absorption spectrum; *2*) and *3*) fluorescence spectra (λ_{exc} = 365 and 412 nm respectively); *4*) and *5*) fluorescence excitation spectra for maxima at 432 and 482 nm respectively.[75]

It has been shown[75] that the solid polymer (XLI) does not fluoresce, while its solutions in DMF are characterised by an intense fluorescence. Fig.10 presents the absorption and fluorescence spectra of solutions of the polymer (XLI)

as well as the fluorescence excitation spectra for λ_{max} = 432 and 482 nm. The dependence of the type of the emission spectrum of the solution on the wavelength of the exciting light indicates the presence of two luminescence centres, which is confirmed by the parameters of the fluorescence excitation spectra. It has been suggested[75] that a short-wavelength luminescence centre with λ_{max} = 432 nm is typical of the polymer (XLI). The long-wavelength luminescence centre with λ_{max} = 482 nm is apparently associated either with the presence in the test solution of polymeric associated species or with the presence of low-molecular-weight admixtures of the type of dianthrylethylene derivatives.[4]

The absence of an appreciable fluorescence of the solid phase can also be explained by the admixture of dianthrylethylenes. A characteristic feature of the molecular structure of dianthrylethylene is that they consist of open chains in which there is steric hindrance to the conjugation of π-electron systems or "overlap zones".[78] The presence of such zones significantly diminishes the intensity of the fluorescence of certain dianthrylethylenes compared with the other anthracene derivatives.

Polymers with two methylene groups between the benzene rings in compound (XLII) have been investigated by absorption and luminescence spectroscopy:[76,77]



(XLII)

They have been synthesised by the reaction of 1,2-dichloroethane with substituted benzenes in the presence of $AlCl_3$ as the catalyst.[79] It has been observed that, together with the band at 260 nm corresponding to the π–π* electronic transition in the benzene ring, the absorption spectra also contain bands in the range 300–400 nm, reflecting the vibronic interaction between the ring and the substituent, as well as the bands in the range 450–500 nm due to intermolecular interaction. It has been observed[76] that the intensity of the π–π* transition in these polymers is determined by the excitation vector, whose magnitude depends on the nature of the substituent R.

Summarising the data on the electronic and vibrational absorption spectra of polyarylenealkyls,[80] the author concludes that, as a consequence of intramolecular and intermolecular interactions, a many-centre type of bond arises in the polymers (XLII). According to the existing ideas,[81] the interpretation of the observed EPR absorption signal in these polymers cannot be accepted as correct and the EPR signal is apparently due to the presence of paramagnetic impurities in the polymer. In view of the foregoing, the author's conclusion[76] that the structure of the polymers (XLII) is intermediate between the conjugated and non-conjugated types also appears to be incorrect.

Kozyreva's study[77] was devoted to the observation of the low-temperature luminescence of the polymers (XLII) in the solid phase and in solutions. The phosphorescence of these compounds has been noted, the decrease of the luminescence intensity during the first instants after the removal of the light source being described by a relation of the hyperbolic and then exponential type. On the basis of data which in our view require revision, the author[77] classifies the polymers (XLII) as crystalline phosphors in terms of the type of their luminescence and suggests that they exist in the liquid crystal state at low temperatures.

Thus the observed spectroscopic properties of polyarylenealkyls are as yet not entirely reliable and require revision. Overall, one should note that the available literature data for the luminescence-spectroscopic properties of carbochain aromatic polymers are fragmentary and require further investigations.

2. Heterochain Aromatic Polymers

The optical properties of heterochain aromatic polymers have been studied in greater detail than the properties of the carbochain polymers. There are literature data obtained in investigations of the luminescence-spectroscopic characteristics of aromatic polyethers,[82] poly-Schiff bases,[83–85] polyamides,[86–89] and polyureas.[86,90]

The study of polyoxy-(2,6-dimethyl)-1,4-phenylene by luminescence spectroscopy showed[82] that it exhibits an intrinsic fluorescence in the form of solutions and films in the ultraviolet region (λ_{max} = 320 nm) and an impurity luminescence in the visible part of the spectrum (λ_{max} = 550 nm), the intensity of the latter diminishing on photolysis of the polymer.

The luminescence-spectroscopic properties of poly-Schiff bases and of model compounds have been investigated by D'Alelio et al[83] and by Vasilenko and co-workers.[84,85] In their studies of the absorption and fluorescence spectra of arylazomethines, Vasilenko and co-workers[84,85] observed that protonation imparts to their molecules a planar configuration and hence diminishes the probability of the radiationless deactivation of the S_1 state. It has been shown[91,92] that the fluorescence process in the free bases of arylazomethines is suppressed by the radiationless internal conversion, whose rate constant has been estimated as 10^{12} s^{-1} for *N*-benzylideneaniline. After comparing the absorption spectra of the hydrocarbon and sulphuric acid solutions of *N*-benzylideneaniline, Vasilenko and co-workers[84,85] concluded that in the protonated form of this molecule the π-electrons are strongly bound and are excluded from the π-electron system of the arylazomethine, as a consequence of which the long-wavelength band in the spectrum of the acid solution undergoes a 25 nm bathochromic shift.

Continuing their investigation of the luminescence-spectroscopic properties of arylazomethines in relation to poly-Schiff bases and a number of model compounds such as the product of the condensation of *m*-phenylenediamine with isophthalic aldehyde [compound (XLIII)] or benzaldehyde [compound (XLIV)] and also the product of the condensation of *p*-phenylenediamine with terephthalic aldehyde [compound (XLV)] or cinnamaldehyde [compound (XLVI)], Vasilenko and co-workers[84,85] observed that the characteristic features of the optical behaviour of *N*-benzylideneaniline discovered in various media persist on passing to more complex systems (Fig.11*a*). Evidently in the case of the solution in sulphuric acid the absorption spectra of the polymer (XLIII) and the model (XLIV) are similar (λ_{max} = 340 nm for the long-wavelength band), whereas for the solution of compound (XLIV) in a non-polar solvent (cyclohexane) λ_{max} = 330 nm.[85] Consequently both the polymers and low-molecular-weight bis(arylazomethine) derivatives are protonated at the nitrogen atoms in sulphuric acid, like *N*-benzylideneaniline, which activates the fluorescence of the test systems.

Fig.11*a* shows that the fluorescence spectra of compounds (XLIII) and (XLIV) are similar and have a resolved vibrational structure with 1300–1000 cm^{-1} gaps between the bands. Analogous conclusions can be reached from the analysis of the absorption and low-temperature fluorescence spectra of the polymer (XLV) and the model (XLVI) (Fig.11*b*). Comparison of the spectra in Figs.11*a* and 11*b* shows that, on passing from the *m*-isomers of the polymeric and model arylazomethines to the *p*-isomers, the long-wavelength

absorption band and all the bands in the fluorescence spectrum are seen to undergo a bathochromic shift; the luminescence intensity of the powdered polymer specimens increases in the same sequence.

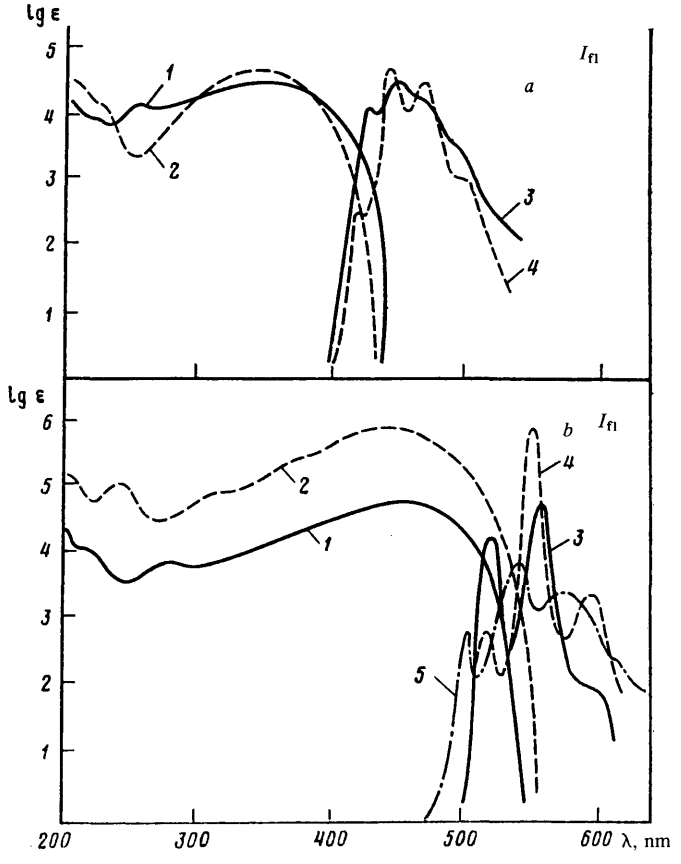
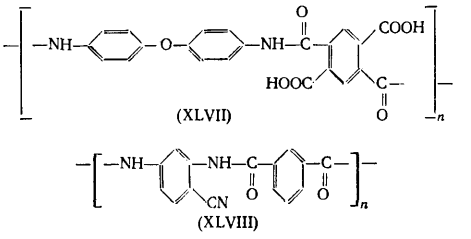


Figure 11. *a*) Absorption spectra at 20 °C (curves *1* and *2*) and fluorescence spectra at −196 °C (curves *3* and *4*) of solutions of the polymer (XLIII) (curves *1* and *3*) and the model (XLIV) (curves *2* and *4*) in concentrated H_2SO_4; *b*) absorption spectra at 20 °C (curves *1* and *2*) and fluorescence spectra at −196 °C (curves *3* and *4*) of solutions of the polymer (XLV) (curves *1* and *3*) and the model (XLVI) (curves *2* and *4*) in H_2SO_4 and the fluorescence spectrum of a powder of the polymer (XLV) at −196 °C (curve *5*).[85]

It is known[93] that the poly-Schiff bases derived from benzil and *p*-phenylenediamine have a resistivity of ~10^{12} Ω cm in the dark and an activation energy for conduction in the range 0.1–0.3 eV. In our view, one of the urgent problems, which have been only partly solved for the low-molecular-weight photoconductors,[94] is the establishment of a correlation between the fluorescence and photoconductivity of the polymer systems.

We shall consider the luminescence properties of aromatic polyamides. It is usually suggested[95] that unsubstituted polyamides of the type of poly-*m*-phenyleneisophthalamide exhibit a blue fluorescence with λ_{max} = 445 nm, caused by the presence of impurities in the polymer. When certain substituents are introduced into the aromatic rings of the polyamides, an intrinsic fluorescence appears. Thus a film of the polyamidoacid (XLVII) fluoresces with λ_{max} = 470 nm, while the polycyanamide (XLVIII) fluoresces with λ_{max} = 425 nm:[96,97]



The first studies on the optical properties of phosphor-containing aromatic polyamides and polyureas date back to the middle 1970's.[86,87,90] The polarised fluorescence of the polyamidoacid (XLIX), containing a luminescent label in the main polymer chain, has been investigated.[87] Unfortunately the authors do not quote data concerning the nature and types of binding of the phosphor fragments in the chain.[87] It is only stated that each label is enclosed between flexible hinged C–O–C junctions and that there is one label for each 300 amidoacid units. The data for solutions of the polymer (XLIX) in DMF and in DMF–glycerol mixtures revealed a linear relation between the reciprocal of the polarisation of the luminescence and T/η, where T is the temperature and η the viscosity of the solvent.

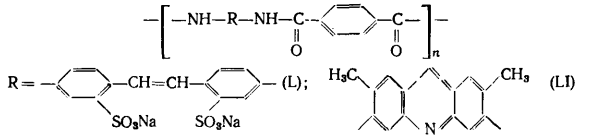
Having calculated the diffusion parameters, the authors[87] concluded that the macromolecules of the polymer (XLIX) exhibit an appreciable kinetic flexibility compared with carbochain polymers. It has been shown that the main inhibiting factor in the kinetically flexible chain of the polyamidoacid is the external viscous friction of the units against solvent molecules.

The synthesis and fluorescence properties of aromatic polyamides and polyureas with three types of phosphor fragments in the chain have been described.[86,90] The polymers were obtained by the interfacial polycondensation of Acridine Yellow, thionine, or the sodium salt of 4,4′-diaminostilbene-2,2′-disulphonic acid with acid dichlorides such as terephthaloyl chloride and sebacyl chloride or with 2,4-tolylene di-isocyanate.

Apart from the synthesis of fluorescent polymers and the comparison of their optical properties with those of the initial phosphor diamines, the authors[86] were also interested in the polyelectrolyte character of all the polyamides and polyureas investigated. The polymers synthesised do not melt up to 300 °C and are soluble in water (polymers with stilbene units in the chain) or in *NN*-dimethylacetamide and DMF (polymers with acridine and thionine units).

A detailed study of the fluorescence properties of the polymer solutions showed that the positions of the maxima in their fluorescence spectra and their fluorescence intensity depend significantly on the concentration of the solution. Thus, for the polymers with stilbene and acridine units, the maximum in the fluorescence spectrum undergoes an appreciable hypsochromic shift (by 20–40 nm depending on the type of polymer) and the concentration of the polymer in solution diminishes from 10^{-3} to 10^{-7} M (calculated in terms of the concentration of phosphor groups). The fluorescence intensity diminishes in the same sequence by a factor of 10–25 for the stilbene-containing polymers and by a factor of 150–300 for the acridine-containing polymers.

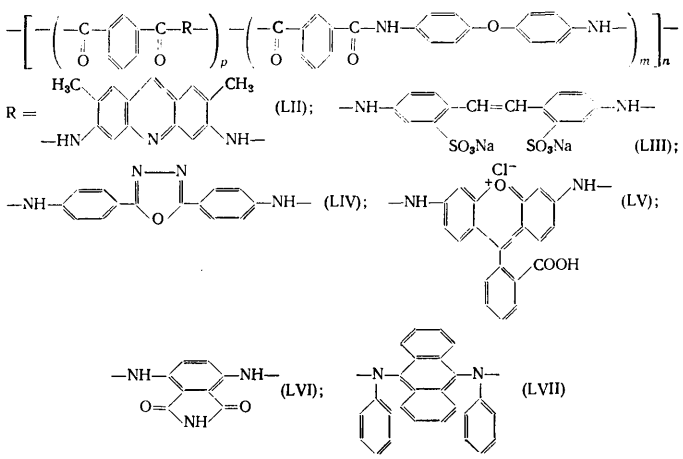
Comparison of the fluorescence characteristics of the initial phosphors and the corresponding polymers showed that the position of the maximum in the fluorescence spectra is determined by the type of polymer. For example, whereas the sodium salt of 4,4'-diaminostilbene-2,2'-disulphonic acid luminesces with λ_{max} = 444 nm in aqueous solution at a concentration of 10^{-4} M, polyureas luminesce with λ_{max} = 440 nm at the same concentration of phosphor groups, while the emission from the dissolved polyamide based on terephthaloyl chloride (L) is at 504 nm:



The authors believe[86] that the appreciable bathochromic shift of the fluorescence band in the spectrum of the last polymer relative to the initial diamine is associated with the increased length of the conjugation chain in it. To a lesser extent, this effect is manifested in acridine-containing polymers: a band with λ_{max} = 510 nm is characteristic of the fluorescence spectra of solutions of the polyamide (LI) based on terephthaloyl chloride (compared with λ_{max} = 500 nm for solutions of Acridine Yellow).

An interesting result of the study of Uno and Kondo[86] is data showing a decreased intensity of the fluorescence of solutions of the polymers (L) and (LI) compared with the solutions of the initial phosphors under ultraviolet irradiation. It was observed that, after irradiation for 1.5 h, the intensity of the fluorescence of solutions of the sodium salt of 4,4'-diaminostilbene-2,2'-disulphonic acid falls by 56.0%, while that of solutions of the corresponding polyamide (L) falls by only 26.7%. For Acridine Yellow and the polyamide (LI), the corresponding figures are 18.4% and 6.5% respectively. The authors[86] correctly attribute the lower photoconductivity of solutions of the stilbene monomer compared with the polymer (L) to the effective *cis–trans* photoisomerisation of the former compound under irradiation conditions. The complete lack of data concerning the absorption and fluorescence spectra of the polymer specimens in the form of films is one of the disadvantages of the study by Uno and Kondo.[86]

Polyamides with a structure similar to that of the polymers described above, containing acridine [polymer (LII)], stilbene [polymer (LIII)], and diphenyloxadiazole [polymer (LIV)] units in the chain have been obtained by the present author and his co-workers:[88,89]



The proposed method of synthesis involving the polycondensation in solution of a mixture of di(aminophenyl) ether and the phosphor diamine with isophthaloyl chloride made it possible to obtain polymers with a fairly high molecular weight, in contrast to interfacial polycondensation.[86,90] Furthermore it permitted the variation of the content of the phosphor groups in the chain within broad limits by altering the ratio of the initial diamines.

The real content of the chromophoric groups in the polyamides (LII) and (LIV) was determined spectrophotometrically—from the intensities of the absorption bands with maxima at 468, 360, and 342 nm respectively.[89] It was found that the experimental concentration of the chromophoric groups is several times lower than expected on the basis of the molar ratios of the diamines used for the polycondensation. The evident cause of this discrepancy is the low reactivity of the initial phosphor diamines, as a result of which a considerable proportion of the latter fail to react.

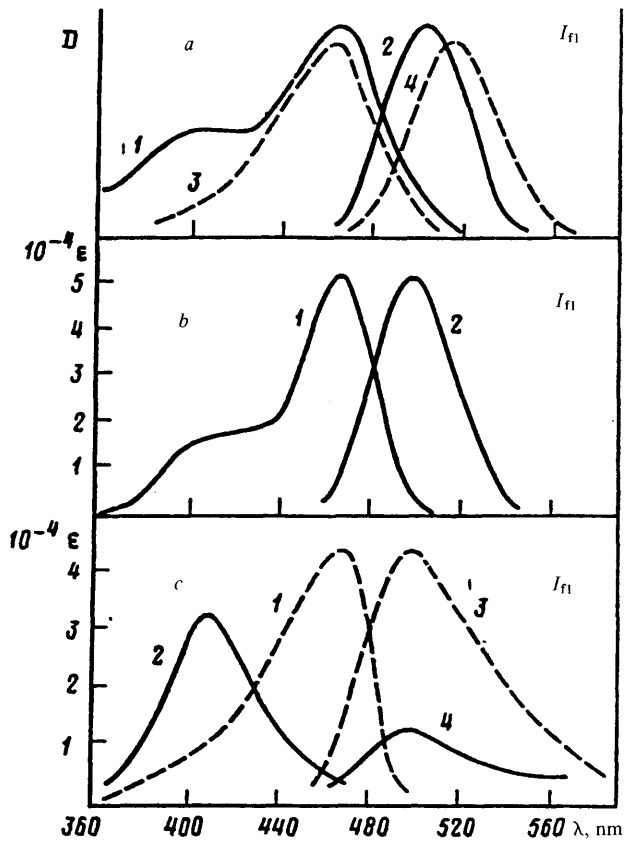
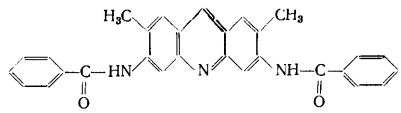


Figure 12. Absorption and fluorescence spectra of acridine-containing compounds: *a*) absorption (curves *1* and *3*) and fluorescence (curves *2* and *4*) spectra of a solution of the polyamide (LII) ($p:m$ = 1:110) in *N*-methylpyrrolidinone (curves *1* and *2*) and in the form of a film (curves *3* and *4*); *b*) absorption (curve *1*) and fluorescence (curve *2*) spectra of a solution of the polymer (LVIII) in *N*-methylpyrrolidinone; *c*) absorption (curves *1* and *2*) and fluorescence (curves *3* and *4*) spectra of solutions of Acridine Yellow in ethanol (curves *1* and *3*) and dimethylformamide (curves *2* and *4*).[89]

Fig.12*a* presents the absorption and fluorescence spectra of the polyamide (LII), with acridine units in the chain, in the form of a film and a solution in *N*-methylpyrrolidinone. The absorption and fluorescence spectra of the model diamide (LVIII) were studied simultaneously (Fig.12*b*).



(LVIII)

It follows from Fig.12 that the long-wavelength absorption and fluorescence bands of the polymer are similar to the corresponding bands of the model compound (LVIII). These data serve as an adequate basis for the assignment of the observed absorption and emission bands of the test polymer to the acridine unit.

The band with the maximum at 410 nm in the absorption spectra of solutions of the polyamide (LII) with acridine units must be attributed to the interchain association of these units. It is known[98] that acridine dyes such as Acridine Yellow tend to self-associate in solutions and the tendency is determined by the nature of the solvent. Thus it has been found that in solutions in DMF the compound is present mainly in the form of associated species characterised by an absorption maximum at 410 nm (Fig.12*b*). In the course of measurements of the absorption spectra of polyamides with different contents of Acridine Yellow fragments, it was found that a decrease in their concentration reduces the optical density ratio D_{410}/D_{465}. Spectroscopic studies of the absorption and fluorescence of solutions and films of polyamides modified by stilbene and diphenyloxadiazole units yielded analogous results.

It follows from data for the fluorescence of polyamide films that the intensity of their emission falls appreciably with increased content of the phosphor groups in the chain, which may be due to both the association of these groups and to the manifestation of the concentration-induced quenching of the fluorescence.[89]

The question of the influence of the phosphor groups in the polyamide chains on the resistance of the latter to ultraviolet irradiation is of independent interest. It is known[99] that the addition of organic phosphors increases in many instances the resistance of polymers to the action of light. After irradiation of polymer films with the unfiltered light of a DRSh-500 lamp for 2 h, it was found that the values of η_{log} for solutions of the polyamides (LII), (LIII), and (LIV) are 74, 85, and 35% respectively relative to the initial value of η_{log}.[89] After the photoageing under the same conditions of a polyamide having an analogous structure but without phosphor groups, η_{log} was found to amount to 61% of the initial value.

It is seen from the data presented that the introduction of acridine and stilbene units increases the photostability of polyamides, while the introduction of diphenyloxadiazole fragments reduces it. A possible explanation of the protective effect of the phosphor fragments may be the fact that the excitation energy of the macromolecules is transferred to these fragments, which have low-lying S_1 levels, and is emitted in the form of the $S_1 \rightarrow S_0$ fluorescence. This protective mechanism may not operate in the diphenyloxadiazole-containing polyamide, where the S_1 levels are too high.

The present author and his co-workers[88,89] synthesised also a whole series of film-forming aromatic polyamides with rhodamine [compound (LV)], 3,6-diaminophthalimide [compound (LVI)], and 9,10-dianilinoanthracene [compound (LVII)] phosphor units, present in the residue of the diamine component, or the 9,10-diphenylanthracene-*pp'*-dicarboxylic acid (LIX) units in the acid component. Most of the features found in the variation of the properties of the polyamides (LII) and (LIII), for example, the increase of η_{log} with decreased content of the phosphor fragments in the chain or the weakening of the fluorescence intensity of the films with increased concentration of these fragments, are also observed with the polyamides (LIV)–(LVII) and (LIX).

As an example, Fig.13 presents the absorption and fluorescence spectra of solutions and films of the polyamides (LVII) and (LIX) and also solutions of the corresponding monomers—9,10-dianilinoanthracene and 9,10-diphenylanthracene-*pp'*-dicarboxylic acid. It follows from the results of the study of the luminescence-spectroscopic properties of these compounds and also the polyamides (LV) and (LVI) and the corresponding monomers that the chromophoric fragments are responsible for the fluorescence and long-wavelength absorption of the polymers (LV)–(LVII) and (LIX).

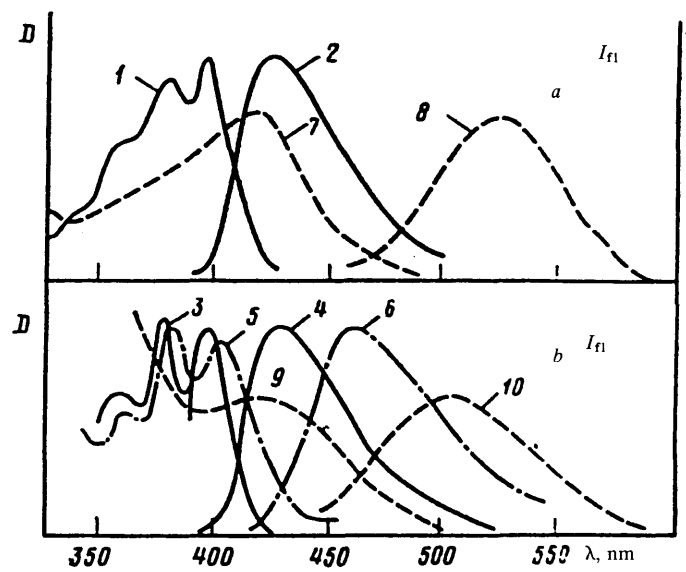


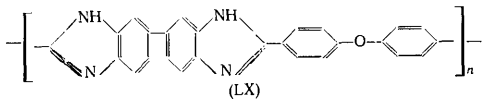
Figure 13. *a*) Absorption (curves *1* and *7*) and emission (curves *2* and *8*) spectra of solutions of 9,10-diphenylanthracene-*pp'*-dicarboxylic acid (curves *1* and *2*) and 9,10-dianilinoanthracene (curves *7* and *8*) in dimethylacetamide; *b*) absorption (curves *3*, *5*, and *9*) and emission (curves *4*, *6*, and *10*) spectra of a film of the polyamide (LIX) (curves *5* and *6*) and solutions in dimethylacetamide of the polyamides (LIX) (curves *3* and *4*) and (LVII) (curves *9* and *10*); for the polyamide (LVII), $p:m = 1:10$.[88]

Certain representatives of the polyamides (LII)–(LIX), capable of forming transparent intensely fluorescent films, are promising as scintillating materials suitable for recording of the tracks of α- and β-particles and neutrons and for X-ray dosimetry.[4]

3. Polyheteroarylenes

Aromatic polymers with a heterocyclic fragment in the chain, which possess very effective mechanical and dielectric properties and a high thermal stability, belong to the class of polymers which have been least investigated from the standpoint of their light absorption and fluorescence properties. There have been only a few studies of the spectroscopic properties of polybenzimidazoles,[100] polybenzoxazoles,[101,102] polyimides,[96,103,104] polyhexazocyclanes,[105] and polymeric bipyridylium salts.[106]

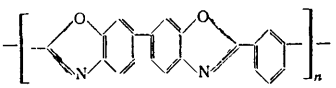
It has been stated in a report[100] that solutions of the polybenzimidazole (LX) in *NN*-dimethylacetamide and formic acid fluoresce in the blue part of the spectrum.



(LX)

The spectroscopic properties of the polymer (LX) were compared with those of the model bis-*p*-(2-benzimidazolyl)-phenyl ether (Fig.14). It was found that the fluorescence of the model is determined by the radiative transitions from the 0–0, 0–1, and 0–2 vibrational levels of the excited ^1L_b state of the benzimidazole ring, while the fluorescence spectrum of the polymer (LX) has a vibrational structure; λ_{max} = 394 and 413 nm. In addition to the monomer luminescence band, the emission spectra of solutions of the polymer (LX) and of the model compound in formic acid contain a longer-wavelength band at 460 nm associated with the fluorescence of the intermolecular associated species, which undergoes a bathochromic shift with increase in the concentration of the solution.

The available information in the literature about the fluorescence properties of polybenzoxazoles is even more scanty. Thus an intense green fluorescence of films of the polymer (LXI) with λ_{max} = 490 and 520 nm has been mentioned;[101,102] the authors confined themselves to the measurement of the emission spectrum without attempting to account for its origin.



(LXI)

The possibility of the fluorescence of aromatic polyimides of different structure has been discussed by the present author and his co-workers.[96,103,104] They showed that, regardless of the presence of phosphor fragments in the chain, the quenching of the fluorescence associated with the nature of the diimide unit is observed in polypyromellitimides. In the study of the spectroscopic characteristics of the model compound *NN'*-dimethylpyromellitimide (LXII) it was observed[96] that this product does not fluoresce at room temperature (in solution) and exhibits an intense phosphorescence at −196°. The absorption and phosphorescence spectroscopic data suggested a scheme for the arrangement of the energy levels in the molecule of (LXII), the characteristic details of which are a low-lying $T_{\pi\pi^*}$ level (20000 cm^{-1}) and the fact that the energy of the $S_{n\pi^*}$ state is intermediate between those of the $S_{\pi\pi^*}$ and $T_{\pi\pi^*}$ states. It is known[69] that molecules with this arrangement of levels do not fluoresce. The quenching of their fluorescence is associated with the probability of a radiationless intersystem crossing from the $S_{n\pi^*}$ level to the $T_{\pi\pi^*}$ level.

The energies of the $S_{n\pi^*}$ and $T_{n\pi^*}$ levels of compound (LXII) can increase on protonation of the pyromellitimide ring. Indeed, it has been shown[96] that in solution in concentrated sulphuric acid the intersystem crossing process becomes unlikely as a consequence of the increase in the energy of the $S_{n\pi^*}$ state, which has been confirmed by the appearance of an intense green fluorescence of compound (LXII) under these conditions.

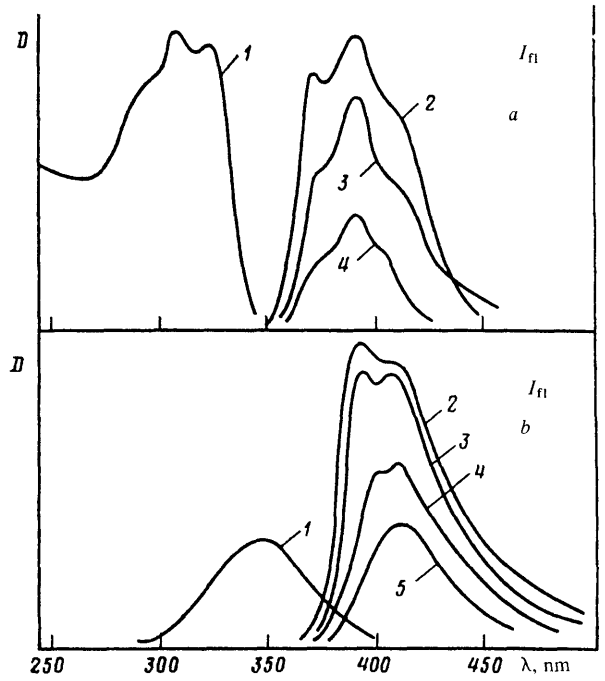
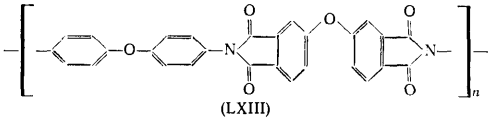


Figure 14. a) Absorption (curve *1*) and fluorescence (curves *2–4*) spectra of solutions of bis-*p*-(2-benzimidazolyl)-phenyl ether in dimethylacetamide at concentrations of 7.9 × 10^{-4} g ml^{-1} (curve *2*), 3.2 × 10^{-3} g ml^{-1} (curve *3*), and 6.3 × 10^{-3} g ml^{-1} (curve *4*); b) absorption (curve *1*) and fluorescence (curves *2–5*) spectra of solutions of the polymer (LX) in dimethylacetamide at concentrations of 4.6 × 10^{-6} g ml^{-1} (curve *2*), 1.5 × 10^{-4} g ml^{-1} (curve *3*), 4.3 × 10^{-4} g ml^{-1} (curve *4*), and 5.2 × 10^{-3} g ml^{-1} (curve *5*).[100]

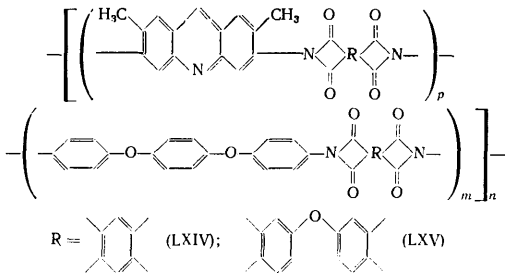
Thus the quenching of the fluorescence in polypyromellitimides is due to the presence of low-lying $n\pi^*$ levels. The appearance of fluorescence in aromatic polyimides requires that a diimide component with higher $S_{n\pi^*}$ and $T_{n\pi^*}$ levels be introduced into their composition. For example, the polyimides based on the dianhydride of oxydi(benzene-3,4-dicarboxylic acid) such as the polymer (LXIII) exhibit an appreciable blue fluorescence:[103]



(LXIII)

A comparative study of the spectroscopic properties of the polypyromellitimides (LXIV) and the polyimides (LXV) with acridine fragments in the chain has been carried out.[104]

The polymers were synthesised by the low-temperature polycondensation of a mixture of Acridine Yellow and the di(4-aminophenyl) ether of hydroquinone with the dianhydrides of the corresponding tetracarboxylic acids with subsequent thermal polycyclodehydration of the prepolymer films:



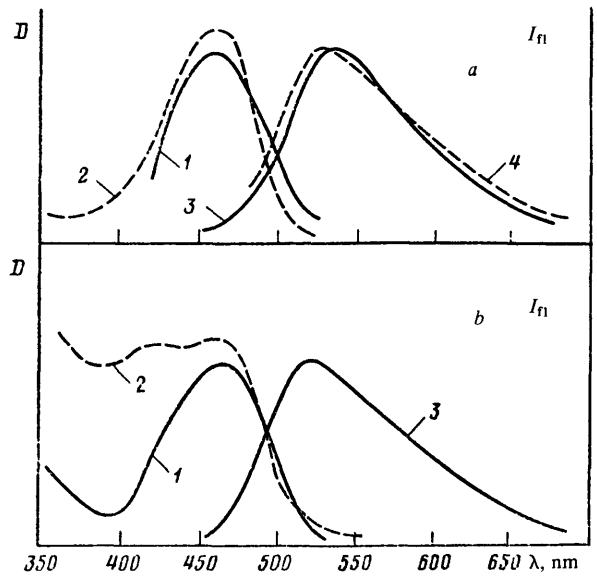
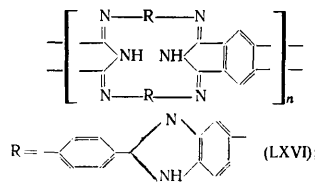
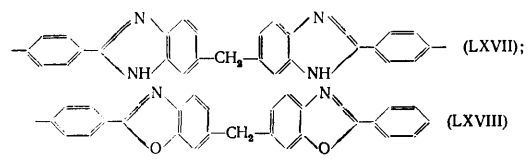


Figure 15. *a*) Absorption (curves *1* and *2*) and emission (curves *3* and *4*) spectra of films of the prepolymer for the polyimide (LXV) (curves *1* and *3*) and the prepolymer for the polyimide (LXIV) (curves *2* and *4*); *b*) absorption (curves *1* and *2*) and emission (curve *3*) spectra of films of the polyimides (LXV) (curves *1* and *3*) and (LXIV) (curve *2*); in all cases $p:m = 1:3$.[104]

Acridine-containing polyamidoacids showed an intense green fluorescence with λ_{max} = 500 nm in solutions and a yellow-green fluorescence with λ_{max} = 530–540 nm in films (Fig.15*a*). Fig.15, which presents the absorption and emission spectra of films of the polyimides (LXIV) and (LXV) as well as the corresponding polyamidoacids, shows that the nature of the dianhydride component has little influence on the spectroscopic properties of the prepolymers. On the other hand, the luminescence-spectroscopic characteristics of the polyimides depend strongly on the character of the diimide fragment (Fig.15*b*). Whereas the absorption spectra of the polyimide (LXV) contain only one band with λ_{max} = 460 nm, in the spectra of the polyimide (LXIV) an absorption band with a maximum at 415 nm, associated with the aggregation of the acridine fragments, appears. Regardless of the ratio $p:m$, all the polyimides (LXV) showed an intense fluorescence with λ_{max} = 515–525 nm, whereas the polyimides (LXIV) did not fluoresce.[104]

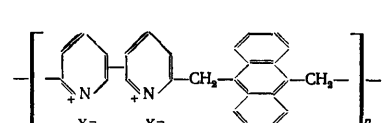
The aim of the synthesis of the acridine-containing polyimide (LXV) as well as other polyheteroarylenes–polyhexazocyclanes (LXVI)–(LXVIII), described by the present author and his co-workers,[105] was the preparation of polymeric phosphors with yellow and orange luminescence, which are of interest for the preparation of scintillating materials:[108]





The polymers (LXVI)–(LXVIII) were synthesised by the polycondensation of pyromellitonitrile with diamines of the phenylbenzimidazole and phenylbenzoxazole series in phenol. It was found that the absorption and fluorescence spectra of these polymers as well as the model hexazocyclanes of analogous structure contain bands in the ultraviolet region associated with the electronic transitions in the phenylbenzimidazole and phenylbenzoxazole fragments; in addition, the fluorescence spectra contain longer-wavelength bands at 540–650 nm associated with charge transfer from the electron-donating chromophoric fragment to the electron-accepting isoindole fragment.

In conclusion we shall consider the absorption and fluorescence properties of polymeric bipyridylium salts (polyviologens) (LXIX), obtained[106] by the Menshutkin reaction of 2,2'- or 4,4'-bipyridyl with 9,10-dihalogenmethylanthracenes in methanol, DMF, or dimethyl sulphoxide at 30–70 °C. The solubility in water and intense fluorescence of these polymers make it possible to use them as luminescent probes for the investigation of biological membranes:[63]



(LXIX)
X=Cl, Br .

The absorption and emission spectra of solutions of the polymers (LXIX) as well as the model (9-methyl)-10-anthrylmethylpyridinium halides (LXX) and the initial 9,10-dihalogenomethylanthracenes (Fig.16) have been investigated. It was found that the absorption spectra of the corresponding chloro- and bromo-compounds have a resolved structure typical for anthracene derivatives; the absorption spectra are fairly close to one another as regards the shape of the bands and their relative positions. On the other hand, appreciable differences were noted in the fluorescence

properties of the monomers, the model compound (LXX), and the polymers (LXIX). Thus, whereas 9,10-dichloromethylanthracene and the corresponding model compound exhibit a weak fluorescence in the crystalline form and in solution, the polyviologens show a bright fluorescence both in the solid state and in solution. Furthermore, 9,10-dibromomethylanthracene and the corresponding model compound do not fluoresce at all either in the solid state or in solution at room temperature, while the bromine-containing polyviologen (LXIX, X = Br) exhibits an intense fluorescence under these conditions.

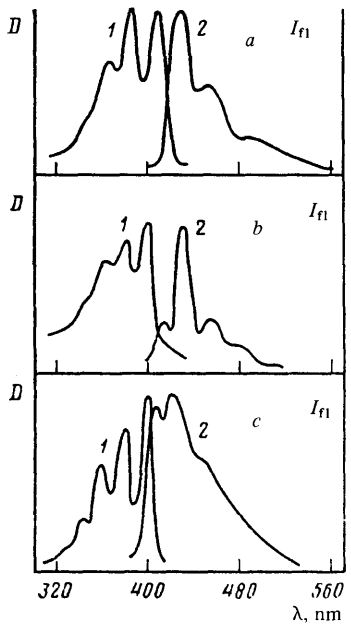


Figure 16. Absorption (curve *1*) and fluorescence (curve *2*) spectra of solutions in dimethylformamide: *a*) of 9,10-dichloromethylanthracene; *b*) of the model compound (LXX, X = Cl); *c*) the polyviologen (LXIX, X = Cl).[106]

The present author and his co-workers[106] suggested as an explanation of the observed differences that in dichloromethylanthracene and especially in dibromomethylanthracene the probability of the radiationless transitions from the S_1 to the T_1 level increases as a consequence of the strong spin–orbital interaction and such transitions are responsible for the quenching of the fluorescence. Halide ions have been detected in polymers in the vicinity of the nitrogen atoms of the bipyridyl residues, which tends to increase the number of vibrational degrees of freedom, reduces the probability of radiationless transitions, and thereby increases the fluorescence quantum yield. The differences between the emission spectra of the polymers (LXIX) and the corresponding model compounds (LXX) are apparently associated with the fact that the bipyridylium salts,[107] which do not contain anthracene fragments, have fluorescence spectra with a set of intense bands in the range 400–450 nm, in contrast to pyridinium salts.

Thus the examples examined above show that, among heterocyclic aromatic polymers, the luminescence-spectroscopic properties have been more or less investigated only for polyimides. The properties of other polyheteroarylenes have been either very little investigated (polybenzimidazoles, polybenzoxazoles, and polyhexazocyclanes) or not at all (polyoxadiazoles, polyquinoxalines, polyquinazolinones, and a whole series of other polymers). At the same time the study of the fluorescence characteristics of these polymers is of undoubted interest, since it is known[4] that many of their low-molecular-weight analogues exhibit an intense fluorescence.

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Summarising the available information about the fluorescence characteristics of condensation polymers, one may conclude that the introduction of phosphor fragments into the composition of the macromolecules can lead to the preparation of materials with an intense luminescence and in many cases with a high photostability and photosensitivity. The specific synthesis of such polymers, which have a high fluorescence quantum yield in the required spectral range, makes it possible to create promising materials for the needs of scintillation and laser technology, for the preparation of migration-resistant luminescent varnishes and dyes, and for medical and biological research. The study of the behaviour of polymers with fluorescent labels in the chain by optical molecular spectroscopic methods enables us to obtain new information, which is either totally unobtainable or obtainable with difficulty by other procedures, about the dynamic mobility of macromolecules in the solution, about the conformational structure of polymers, etc.

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Functional Derivatives of Polyisobutene

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The methods of synthesis of isobutene polymers with end groups of different types are examined. It is shown that advances in the synthesis of these compounds are associated with the progress in the field of the regulation of the cationic polymerisation and copolymerisation of isobutene and the degradation of isobutene polymers and copolymers. Examples of the employment of functional derivatives of isobutene polymers in various branches of technology are presented. The bibliography includes 102 references.

CONTENTS

I. Introduction 710
II. Methods for the introduction of functional groups into isobutene polymers during polymerisation 710
III. Degradation as a method of synthesis of functional derivatives of isobutene polymers 714
IV. Reactions of isobutene polymers via end groups 716
V. Applications of the functional derivatives of isobutene polymers 718

I. INTRODUCTION

Polyisobutene (PIB) and its copolymers (PIBC) together with dienes occupy an outstanding position among polyolefins as regards the volume in which they are manufactured and used. This is due to the availability of the raw materials and the valuable properties of the polymer. "Defect-free" PIB molecules exhibit a relatively high resistance to chemical and physical influences and are irreplaceable as corrosion resistant hermetic sealing compounds, additives, oils, and other materials.[1] On the other hand, the chemical inertness of PIB hinders the introduction of functional groups into the polymer chain. It is known that the introduction of such groups significantly expands the applications of hydrocarbon elastomers to which PIB also belongs.[2]

During the last 5–10 years numerous publications devoted to the synthesis of PIB with specified end groups by the cationic polymerisation of isobutene (IB), oxidative degradation of PIBC with dienes, and other procedures have appeared. The introduction of reactive groups into PIB and their subsequent reactions lead to the formation of products with polar groups, for example, with antioxidant fragments, graft and block copolymers, etc. i.e. to the variation of the properties of PIB over a wide range of molecular weights. This leads to new applications of PIB.

The aim of this review is the systematic account and a survey of the literature data concerning the method of synthesis of functional derivatives of PIB with specified end groups and new applications of the modified PIB.

II. METHODS FOR THE INTRODUCTION OF FUNCTIONAL GROUPS INTO ISOBUTENE POLYMERS DURING POLYMERISATION

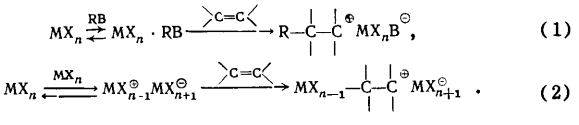
Until recently it was believed that the PIB obtained by the polymerisation of IB under the influence of acid catalysts contain mainly t-butyl and unsaturated fragments at the end of the chain.[3] However, the latest investigations of the low-temperature cationic polymerisation of IB in the presence of complex catalysts and (or) specially introduced additives indicated the possibility of forming PIB with end groups different from those indicated above.[4] Here and henceforth these products are treated as functional derivatives of PIB. In terms of their origin, the end groups in PIB can be divided by convention into "head" groups (formed in the polymer chain initiation and transfer stages), and "tail" groups (formed in chain termination steps). Serious obstacles to the introduction of functional groups into PIB during the cationic polymerisation of IB arise from the high reactivity of the intermediate carbonium ions, the high fluidity, and the difficulty of controlling the PIB formation processes. The short lifetime of the carbonium ion centres rules out the possibility of polymerisation via the "living chain" mechanism,[5] which is the traditional method for the introduction of tail functional groups into polymers based on anionically active monomers.[6,7]

The synthesis of PIB with specified end groups was a consequence of a deeper understanding of the mechanism of the cationic polymerisation of IB and, in particular, of the chemistry of the chain initiation and termination reactions, as well as the application of modern methods for the quantitative analysis of polymers.

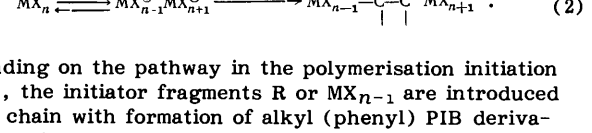
In contrast to Brønsted acids, which lead to the formation of low-molecular-weight products alone[3] and carboxylate salts which are relatively inactive in polymerisation,[4] Lewis acids and complexes based on them show a high reactivity in the polymerisation of IB, creating difficulties in the regulation of the process as a whole and of its individual elementary stages.

When strong Lewis acids (MX_n) are used as the catalyst, their interaction with the monomers and additives (the cocatalyst RB) determines the different initiation pathways and hence also the nature of the head groups (Scheme 1).

Scheme 1



(1)



(2)

Depending on the pathway in the polymerisation initiation reaction, the initiator fragments R or MX_{n-1} are introduced into the chain with formation of alkyl (phenyl) PIB derivatives [reaction (1)] or polymeric organometallic compounds [reaction (2)] respectively. The predominance of a particular reaction pathway depends on the nature of the Lewis acid, the cocatalyst, their concentrations, and the polymerisation conditions.[4] As a rule, these reactions occur under conditions which absolutely rule out the presence of traces of proton-donating compounds in the system. However, such purity has been achieved only in isolated studies using

special vacuum apparatus and the most sophisticated experimental techniques.[4,8,9] In the polymerisation of IB in the presence of traditional catalysts ($AlCl_3$ and BF_3 containing admixtures of proton donors HB) the head t-butyl groups are formed both in the initiation of the process by protons [reaction (1)] and in the chain transfer to the monomer [reaction (2)] while the tail C–C bonds arise only in the chain termination by reactions (3) (Scheme 2).

Scheme 2

$$HB + MX_n + C_4H_8 \rightarrow \quad t\text{-}C_4H_9^{\oplus}MX_nB^{\ominus}, \qquad (1)$$

$$t\text{-}C_4H_9^{\oplus}MX_nB^{\ominus} + nC_4H_8 \rightarrow \quad t\text{-}C_4H_9(C_4H_8)_n^{\oplus}MX_nB^{\ominus}, \qquad (2)$$

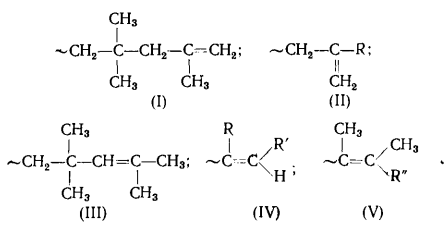
$$t\text{-}C_4H_9(C_4H_8)_n^{\oplus}MX_nB^{\ominus} + C_4H_8 \rightarrow \quad t\text{-}C_4H_9(C_4H_8)_kC_4H_7 + \quad t\text{-}C_4H_9^{\oplus}MX_nB^{\ominus}, \qquad (3)$$

where reactions (1), (2), and (3) are elementary initiation, propagation, and termination steps and $k = n - 1$.

Since reactions (1) and (3) take place even when aprotic cocatalysts are used (Cl_2, RCl, etc.[4]), the introduction of head groups other than t-butyl groups into PIB presents certain difficulties associated both with the elimination of the influence of proton-donating impurities and with the selection of catalytic systems or additives which prevent chain transfer to the monomer.

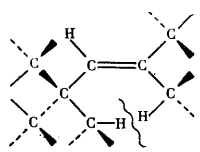
Bearing in mind the decisive contribution of the polymer chain termination reaction to the formation of head and tail groups in PIB,[9,10] it is useful to consider the characteristic features of this reaction.

A characteristic feature of the cationic polymerisation of IB in the presence of the majority of acid catalysts is intense chain transfer to the monomer [reaction (2), Scheme 2].[8] Quantitative and qualitative analysis of the end groups in PIB established that on average there is one C=C bond per macromolecule.[11,12] According to ^1H NMR data,[12] the unsaturated groups in PIB can be represented by structures (I)–(V) with structures (III) and (IV) predominating:



These results significantly supplement and correct the investigations in which mainly vinylidene C=C bonds were detected by infrared spectroscopy.[13]

The ratio of trisubstituted and vinylidene C=C bonds in IB dimerisation and trimerisation processes is probably controlled by steric factors.[9] The transition state in the formation of structure (III) is slightly compressed owing to the interaction of the hydrogen atoms of the methyl groups not linked by chemical bonds:



The two hydrogen atoms shown below this scheme tend to approach one another as soon as a double bond is formed. In contrast to this, the transition state in the formation of structure (I) is much less deformed, which compensates for the difference between the heats of formation of the olefins. When the internal stress cannot be relieved by the rotation of the interaction groups, compound (I) is formed in this case as the main product (Table 1).

Table 1. Characteristics of unsaturated PIB.

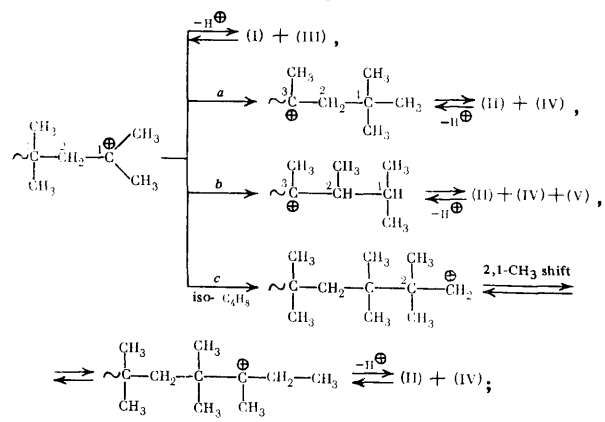
Catalyst + additive	M_n^*	Content of C=C bonds, % of theoretical		Method of determination**	Refs.
		tri-substituted	vinylidene		
H_2SO_4(KY-2)	412	20	80	1	[9]
$CuSO_4$·HCl	468	60	40	1,3	[10]
$CaSO_4$·CCl_3CO_2H	880	46	45	1	[12]
BF_3	1950	46	30	1	[12]
BF_3·CH_3COOH	590	40	29	1	[12]
BF_3·H_2O	970	51	43	1	[12]
$AlCl_3$	770	67	9	1,2	[12]
RCl–BCl_3–$CH_3CN(C_2H_5)_2$	500	0	100	1	[14]

*M_n represents the number-average molecular weights of the PIB.
**1) ^1H NMR; 2) infrared spectroscopy; 3) ozonolysis.

Depending on the polymerisation conditions and the nature of the catalysts, the ratio of the trisubstituted and vinylidene double bonds in PIB varies within wide limits.

Compounds (I) and (III), formed initially in the PIB obtained in the presence of BF_3, can probably undergo a skeletal rearrangement and isomerisation to compounds (II), (IV), and (V) (Scheme 3, *a* and *b*), which agrees with the results of studies of the model system tri-isobutylene + $AlBr_3$ + DBr.[15] The conclusion that compound (V) is formed is based on the fact that the unsaturation detected by ^1H NMR (which is insensitive to tetrasubstituted C=C bonds) is much less marked than the unsaturation measured by hydrogenation methods. The low content of vinylidene C=C bonds and the predominance of compound (IV) among the trisubstituted olefins in the PIB obtained in the presence of $AlCl_3$ are probably associated with multistage polymer chain termination. According to Puskas et al.[12] and Slobodin and Matusevich,[16] it includes the anomalous "tail to tail" addition of isobutene and the subsequent methyl shift (Scheme 3, *c*).

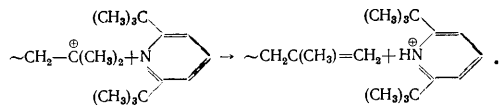
Scheme 3



a) 1,3-CH_3 shift; *b*) 1,2-H and 1,2-CH_3 shifts; *c*) anomalous "tail to tail" addition of isobutene; the symbol ~ denotes the PIB chain.

The anomalously high content of compound (I) in the PIB obtained in the presence of 2,6-di-t-butylpyridine (Table 1) is a consequence of the complete suppression of the reaction involving chain transfer to the monomer. The aromatic base then serves as a kind of trap,[17,18] which selectively abstracts a proton from the CH_3 group of the growing carbonium ion and does not interact with the sterically less accessible protons of the CH_2 groups (Scheme 4).

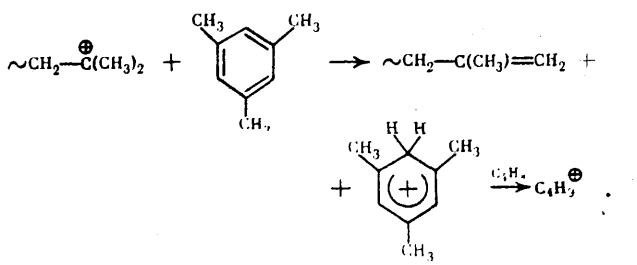
Scheme 4



Apart from its influence on the character of the terminal double bonds, 2,6-di-t-butylpyridine promotes an increase of the molecular weight of the PIB (by an order of magnitude) and a narrowing of its polydispersity (by a factor of 2–3).

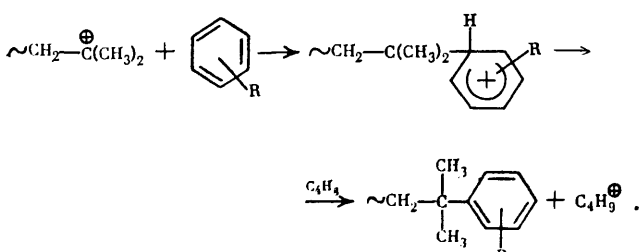
Other sterically hindered aromatic compounds such as 2,4,6-tri-t-butylphenol[19] and 1,3,5-trimethylbenzene[20] can behave in the isobutene polymerisation reaction as mediators in the chain transfer step to the monomer in accordance with Scheme 5 and can broaden the molecular weight distribution.

Scheme 5



In the polymerisation of isobutene in the presence of anisole,[21] 2-alkyl- and 2,4-dialkyl-phenols,[19,22] and certain methylbenzenes,[20] the chain transfer to the monomer is accompanied by the alkylation of the aromatic compounds by the growing carbonium ion with formation of aromatic polyisobutene compounds in accordance with Scheme 6:

Scheme 6



The molecular weight of the functional PIB derivatives is determined by the process temperature and varies from 400 to 200000. The relative contents of the unsaturated and aromatic groups in PIB depends on the ratio of the rates of the competing reactions, which is to a large extent determined by the nature of the catalyst and of the aromatic hydrocarbon (Table 2).

The relative rate constants for the transfer of the polymer chain to methylbenzenes increase with increasing basicity of the aromatic hydrocarbons in the sequence toluene < *m*-xylene < hemimellitol.[20] The presence of aromatic fragments in PIB has been demonstrated by ^1H and ^{13}C NMR and by the EPR of the phenoxy-radicals, obtained on oxidation of the polymers by PbO_2,[19] and by ultraviolet spectroscopy in combination with gel-permeation chromatography.[22] The maximum content of the aromatic end groups in the products has been obtained by polymerisation in the presence of 2,6-dialkylphenols.[19] The contribution of the alkylation reaction increases at lower temperatures and in the presence of the $SnCl_4$ catalyst it becomes dominant.

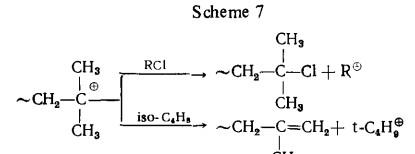
Table 2. Methods of synthesis of polyisobutene with aromatic end fragments at −78 °C.

Catalyst	Reaction conditions		10^{-4} MW*	Relative content of tail groups in PIB, %		Refs.
	aromatic hydrocarbon	solvent		C=C	Ar **	
$(CH_3)_2AlCl$	$C_6H_5CH_3$***	toluene	0.1	90	10	[23]
$C_2H_5AlCl_2$	$C_6H_5CH_3$	toluene	8.5	50	50	[20]
$C_2H_5AlCl_2 \cdot HCl$	$C_6H_5CH_3$	toluene	5.9	40	60	[20]
$C_2H_5AlCl_2 \cdot H_2O$	$C_6H_5CH_3$	toluene	5.1	40	60	[20]
$3C_6H\text{-}CH_3 \cdot 2AlCl_3 \cdot HCl$	$C_6H_5CH_3$	toluene	0.9	20	80	[20]
$AlCl_3(SnCl_4)$	2,6-dimethylphenol	chloroethane	1.1	0	100	[19]
$AlCl_3(SnCl_4)$	2,3,5,6-tetramethylphenol	chloroethane	—	40	60	[19]
$AlCl_3(SnCl_4)$	2,6-di-isopropylphenol	chloroethane	—	—	90	[19]
$AlCl_3(SnCl_4)$	2,6-di-t-butylphenol	chloroethane	0.7	—	99	[19]
$AlCl_3(SnCl_4)$	2-methylphenol	chloroethane	—	—	2.4	[19]
$AlCl_3(SnCl_4)$	phenol		—	—	2.2	[19]
$AlCl_3+SOCl_2$	2-s-butylphenol****	methyl chloride	0.3	—	19.8	[22]
$AlCl_3+SOCl_2$	2-s-butylphenol****	heptane	0.46	—	32.5	[22]

*MW = molecular weight. **Ar = aromatic fragments.
+25 °C. *−70 °C.

Another example of the use of reactions involving chain transfer to a specially introduced reagent in order to obtain a tail functional group other than an unsaturated group (suppression of chain transfer to the monomer) is provided by the polymerisation of IB in the presence of alkyl chlorides. As in the case of aromatic compounds,[20] alkyl chlorides participate in the competitive (relative to the monomer) interaction with the growing centre, leading to the formation of PIB with end fragments in accordance with Scheme 7:

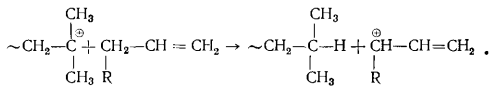
Scheme 7



The ratio of the products[24] is determined by the relative concentrations of RCl and the monomer and by the rate constants for the corresponding reactions. However, the increase in the concentration of RCl entails not only an increase in the chlorine content in the polymer with retention of a high yield of the product[25] but also a significant decrease of its molecular weight. In contrast to RCl (a pure chain transfer agent), α-olefins (chain terminating agents) do not

influence the molecular weight of the product, but significantly reduce the yield (the length of the kinetic chain) as a consequence of the allyl termination reaction[26] with formation of saturated PIB in accordance with Scheme 8:

Scheme 8



Many compounds exhibit both effects to a greater or lesser extent, the effects being quantitatively expressed in terms of empirical poisoning and chain transfer coefficients (Table 3). The knowledge of these quantities provide valuable information about the character of the polymer chain termination reaction under the influence of various additives, which determine the number, size, and nature of the end groups in the PIB molecules formed.

Table 3. Empirical chain transfer and poisoning coefficients in the synthesis of functional derivatives of PIB.[27]*

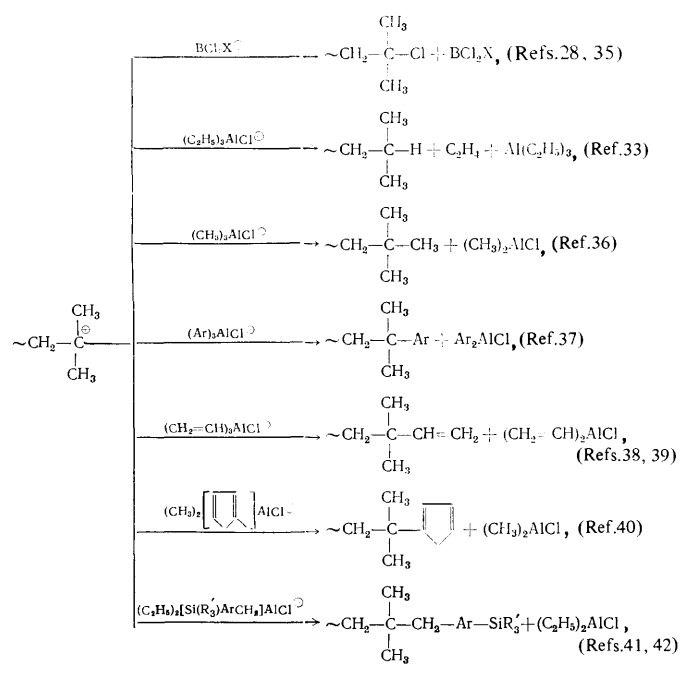
Compound	Coefficients	
	poisoning	chain transfer
Propene	4.9	0
But-1-ene	6.2	0
Pent-1-ene	9.7	0
Hex-1-ene	11.9	0
Oct-2-ene	20.8	12.1
Butadiene	7.6	2.0
2,5-Dimethylhexa-2,4-diene	26.7	15.2
2,3-Dimethylbuta-1,3-diene	107	26
Cyclohexadiene	103	48
Isoprene	140	60
Piperylene	170	327
Cyclopentadiene	900	—
2-Methylcyclopentadiene	685	—
Cyclohexene	5.3	2.7
Cyclo-octone	11	31.2
Cyclopentene	16.3	27
1-Methylcyclohexene	14.7	43.4
1-Methylcycloheptene	66.7	540
1-Methylcyclopentene	280	286
2-Methylpent-1-ene	3.5	53.8
2-Ethylhex-1-ene	24.7	248
2,4,4-Trimethylpent-1-ene	66.7	700
2,4,4-Trimethylpent-2-ene	66.7	34.6
3-Methylbut-1-ene	0	0
4-Methylpent-1-ene	2.9	0
3,3-Dimethylbut-1-ene	0	0
Vinylcyclohexene	3.7	6.7
Indan	10.8	—
Indene	99	210
Norbornene	19.4	57.2
Norbornadiene	16	0
1,5-Cyclo-octadiene	9	1.8
Allyl chloride	0	6.2
Methylallyl chloride	1.6	6.9
2-Chlorobutadiene	6.6	24.5
Crotyl chloride	11.2	27.5
Isopropyl chloride	0	0
Isobutyl chloride	12.5	13.4
t-Butyl chloride	4.4	75.7
Isopropyl bromide	0	0
Isobutyl bromide	1.8	15
t-Butyl bromide	3.5	71.4

*Initiator—$AlCl_3$ in CH_3Cl; solvent—n-pentane; −78 °C.

Wider possibilities, from the standpoint of the preparation of functional PIB derivatives, arise from the chain termination reaction at the initiator fragment. Depending on the nature of the complex initiator $MX_n + R^{\delta+}B^{\delta-}$, one distinguishes termination by a Lewis acid fragment X (for the systems $BCl_3 + H_2O$,[28] $R_2AlCl + RCl$,[28] and $R_2AlCl + Cl_2$ [29]) and termination by the cocatalyst B fragment (for the combination $TiCl_4 + H_2O$, $TiCl_4 + CCl_3COOH$, and $SnCl_4 + C_6H_5OH$ [4,30,31]). The pathways followed in the above polymer chain termination reactions depend on the strength of the donor–acceptor interactions of the components of the initiating system. When it is high ($BF_3 + H_2O$), chain transfer to the monomer with retention of the BF_3OH^- counterion is preferable, as stated above.[12] With decrease in the stability of the complex initiators (based on titanium and tin compounds), the initiation and chain termination proceed with participation of the activated Lewis acid RB, i.e. the cocatalyst behaves as a kind of telogen, forming head and tail groups in the PIB. An additional complexity from the standpoint of the formation of end groups of a specified kind is introduced by systems of the type indicated above, which permit different pathways in the fragmentation of RB, for example, the dissociation of the C–O and O–H bonds in ROH.[32]

Comparison of the experimental and calculated (quantum-chemical analysis of the $\equiv C^+$ or MX_n complex with alcohols by the CNDO/2 method in terms of the Santry–Pople–Segal parametrisation) data shows that the pathway in the fragmentation of ROH bound in a complex depends on the nature of R and the strength of the acid. An increase in the acidity of MX_n and in the degree of branching of the group R promotes the preferential fragmentation of the alcohol at the C–O bond with incorporation of the OH group in the polymer.[32] For $SnCl_4 + C_6H_5OH$,[31] chain termination via the elimination of phenoxy-groups is determined primarily by the effect of the $(p-p)_\pi$ conjugation of the oxygen atom with the aromatic ring, which hinders the rupture of the C(phenyl)–oxygen bond. Since the elimination of the ligands from the MX_nB^- counterion depends on the energy of their binding to the metal and on the stability of the Lewis acid formed, it is possible for the ligand X to be eliminated and then incorporated in the polymer chain in the form of an end group. Reactions of this type occur when relatively weak Lewis acids (BCl_3, R_2AlCl) are used as initiating systems.[28] Numerous model investigations carried out on di- and triisobutenes[33] in the presence of catalysts–cocatalyst systems[34] and also the results of the physicochemical analysis of the polymers established that Cl and R are eliminated from the $[BCl_3R]^-$ and $[R_3AlCl]^-$ counterions respectively in accordance with the scheme:

Scheme 9



where X = OH, Cl, etc., R′ are alkyl radicals, and Ar are fragments of aromatic hydrocarbons.

Because of the absence of chain transfer to IB, the use of these catalysts in absolutely dry systems leads to extensive possibilities not only for the introduction of the specified tail groups into the PIB but also for the synthesis of PIB with functional head groups. The combination of controlled initiation and chain termination methods in the polymerisation of isobutene leads to monofunctional and αω-bifunctional PIB depending on the conditions[37] (Table 4).

Table 4. The synthesis of certain αω-bifunctional PIB.

Initiating system	T, °C	10^{-3}MW of PIB	αω-Bifunctional PIB	Refs.
Cl_2+BCl_3	−40 — −100	—	$Cl-CH_2-C(CH_3)_2-PIB-CH_2-C(CH_3)_2-Cl$	[43]
$CH_2=CH-CH(CH_3)Cl+Al(CH=CH_2)_3$	−30 — −75	—	$CH_2=CH-CH(CH_3)-PIB-CH=CH_2$	[38]
$(CH_3)_2C=CH-CH_2Cl+BCl_3$	−50	9.3—14.3	$(CH_3)_2C=CH-CH_2-PIB-C(CH_3)_2Cl$	[44]
$Cl-C(CH_3)_2-(CH_2)_3-C(CH_3)_2-Cl+(C_6H_5)_3Al$	−10 — −70	9.0—22.0	$C_6H_5-PIB-C_6H_5$	[45]
$Cl-C(CH_3)_2-C_6H_4-C(CH_3)_2-Cl+BCl_3$	−30 — −70	3.1—100.0	$Cl-C(CH_3)_2-CH_2-PIB-C(CH_3)_2-C_6H_4-C(CH_3)_2-PIB-CH_2-C(CH_3)_2-Cl$	[46, 47]

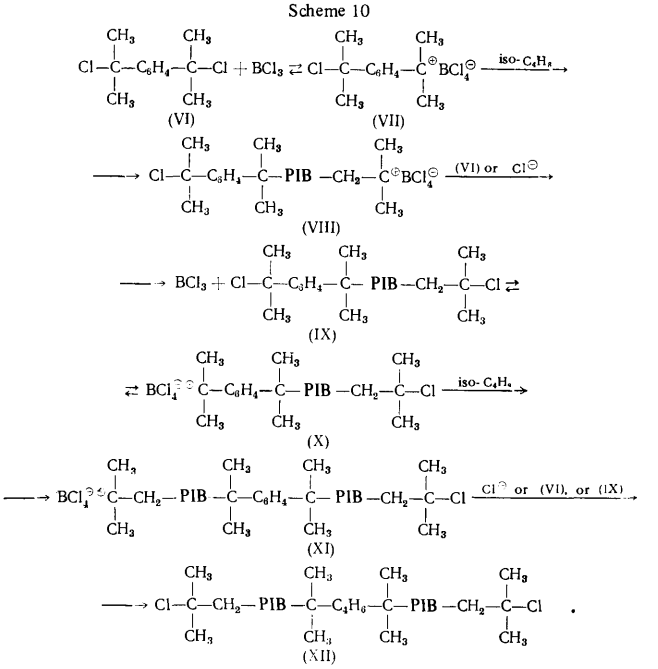
The formation reactions of αω-divinyl-PIB, and α-chloro-ω-vinyl-PIB are based on the principle of controlled chain initiation and termination by the Cl, $CH_2=CH-CH(CH_3)$, and $(CH_3)_2C=CH-CH_2$ cations in the first stage and fragment anions Cl and $CH=CH_2$ in the second respectively. It has been shown[38] that in such cases polymerisation is initiated slowly owing to the greater stability of the primary cationic species compared with the growing PIB carbonium ion. In contrast to the systems indicated, the dihalides combine the functions of the initiator and chain transfer agent. The degree of chain transfer to the monomer in the system is slight, while chain transfer to *p*-bicumenyl chloride is the dominant polymer chain termination reaction.[48,49]

The reactions (Scheme 10) result in the formation of bifunctional PIB containing in the middle of the chain one *p*-phenylene group and two terminal Cl atoms.[46]

The scheme for the formation of αω-dichloro-PIB resembles the cationic telomerisation reaction of isobutene,[50—52] but the products differ by significantly higher molecular weights and have a narrow molecular weight distribution with a width of 1.46—1.70.[47,53]

It is noteworthy that a number of patents deal with the synthesis of PIB having specified end groups. However, owing to the lack of a detailed specification of the experimental conditions, their value is reduced and they are therefore not quoted here.

Scheme 10

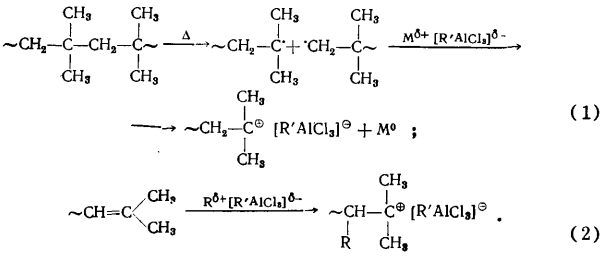


III. DEGRADATION AS A METHOD OF SYNTHESIS OF FUNCTIONAL DERIVATIVES OF ISOBUTENE POLYMERS

The degradation of PIB and PIBC was investigated previously only with the aim of demonstrating the structure (composition) of the compounds[54,55] or to estimate the stability of PIB in relation to various physical influences.[56—58] The free-radical decomposition of PIB proceeds with formation of a complex range of products.[59,60] Furthermore, specific degradation of polymers can serve as a convenient method of synthesis of functional PIB.

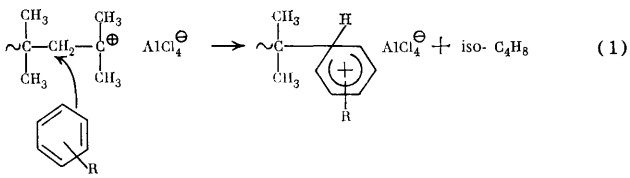
The thermocatalytic degradation of PIB via a mechanism involving depolymerisation under the influence of aluminium chloride complexes has been described.[61—63] Depending on the conditions, it is initiated in accordance with a "random law" via the homolytic dissociation of a C—C bond of the polymer with subsequent redox interaction of the polymer radical and the cation of the complex [Scheme (11), reaction (1)] or in accordance with the "end group" law via the interaction of the complex with the terminal C—C bond of the polymer [reaction (2)]:

Scheme 11

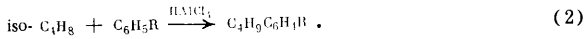


The reaction obeys the general rules for electrophilic processes and in the presence of aromatic hydrocarbons can take place at temperatures below the ceiling temperature for the decomposition of PIB, which is 50 °C.[64-66] The study of the decomposition of PIB in the range from -78° to 200 °C, catalysed by aluminium chloride, showed[64] that the polymer with terminal C=C and C–Cl bonds undergoes degradation from the end of the chain in the presence of ring-alkylating methyl- and isopropyl-benzenes with formation of aromatic polyisobutylene compounds having the general formula $C_4H_9(C_4H_8)_{6-10}C_6H_4$ and t-butyl derivatives of alkylbenzenes. The activating role of the aromatic hydrocarbon in reducing the PIB decomposition temperature below the limiting temperature apparently consists in promoting the fragmentation of the PIB macrocations at the preterminal C–C bond in the coupled alkylation reaction [Scheme 12, reaction (1)] and in binding the IB evolved by alkylating the alkylbenzene with the olefin [reaction (2)]:

Scheme 12



(1)



(2)

When sterically hindered aromatic compounds (mesitylene, tri-isopropylbenzene) are used and also when the reactions are carried out in the absence of alkylbenzenes, the PIB remains indifferent to the action of an acid catalyst under the experimental conditions at temperatures below 50 °C.[64]

More extensive possibilities for the introduction of functional groups into PIB in the degradation process arise from the oxidative cleavage of polymers or copolymers with dienes either at the C=C bonds[67,68] or at the aromatic fragment in the centre of the PIB chain[69] (Table 5).

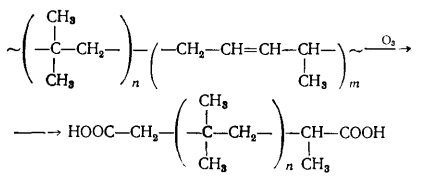
Table 5. The synthesis of αω-bifunctional PIB derivatives by the oxidative cleavage of polymers.

Polymer	Oxidant	Functional derivative	Refs.
$C_6H_{6-n}[C(CH_3)_2$— PIB —$C(CH_3)_2$·.Cl]$_n$, where n = 2, 3	$CF_3COOH-H_2O_2$	HOOC— PIB —COOH	[69]
Isobutene-piperylene copolymer	O_3 + pyridine	HOOC— PIB —COOH	[67, 70]
Ditto	O_3	OCH— PIB —COOH	[71]
"	RuO_4 + co-oxidant	HOOC— PIB —COOH	[72]
Isobutene-2,3-dimethylbuta-1,3-diene copolymer	RuO_4 + co-oxidant	CH_3—C(=O)— PIB —C(=O)—CH_3	[72]
Isobutene-isoprene copolymer	O_3	CH_3—C(=O)— PIB —COOH	[69]

The oxidation of linear and three-arm star PIB having the general formula $C_6H_{6-n}[C(CH_3)_2$–PIB–$C(CH_3)_2Cl]_n$, where n = 2 or 3, with the $CF_3COOH-H_2O_2$ mixture in the CCl_4-H_2O two-phase system at 60 °C lowers the molecular weight of the polymer by a factor of two (for n = 2) or three (for n = 3) as a result of the cleavage of the aromatic ring and the formation of PIB with terminal ~COOH groups.[69]

When high-molecular-weight PIBC, containing 2–4 wt.% of piperylene, are ozonised in the presence of pyridine, PIB with molecular weights of 1800–4000, containing up to 1.8 COOH groups per macromolecule, are formed[67] in accordance with the scheme:

Scheme 13



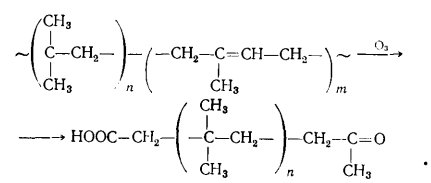
The preparation of these products includes three stages: (1) cleavage of the double bonds with formation of aldehyde and acid groups; (2) oxidation of the aldehydes to acids and peracids; (3) reduction of the peracids to acids.

For the process to be selective, it is necessary to maintain an equimolar ratio of ozone to the diene fragments in the polymer. When this ratio is disturbed, either the degradation of the isobutene chain takes place in the presence of an excess of ozone or the copolymer undergoes incomplete degradation at the diene units if there is insufficient oxidant.[73]

In the controlled ozonisation of PIBC with piperylene in the absence of pyridine, aldehydoacids are formed,[71] while in the presence of pyridine the products are dicarboxylic.[67, 68,70] As a result of a detailed study of the ozonolytic degradation of PIBC with piperylene, the Enjay Company (USA) developed the industrial manufacture of liquid PIB with terminal carboxy-groups.[67] The nature of the terminal functional groups introduced into PIB by this method is determined not only by the ozonolysis conditions but also by the type of the diene fragment in the copolymer.[68]

When isobutene copolymers are ozonised with subsequent thermal decomposition of the ozonides, ketoacids are formed[74] via the scheme

Scheme 14



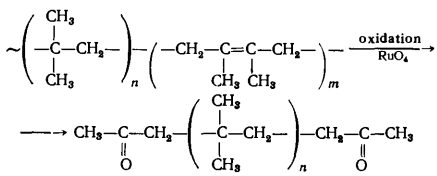
A decrease in the electronegativity of the substituent at the double bond in the copolymer increases its reactivity with respect to ozone (Table 6).

Table 6. The rate constants for the addition of ozone to the double bond in PIBC with dienes.[74]

Copolymer	10^{-5} k, litre mole^{-1} s^{-1}
PIBC with isoprene	10.0
PIBC with penta-1,3-diene	2.9
Brominated PIBC with isoprene	1.0
Chlorinated PIBC with isoprene	0.8

For example, the preparative possibilities of the synthesis of functional PIB derivatives in the course of oxidative degradation are extended when PIBC with 2,3-dimethylbuta-1,3-diene are used. [72] Their oxidation in the presence of catalytic amounts of RuO_4 gives rise to almost quantitative yields of diketones (Scheme 15):

Scheme 15



When the distribution of diene units with the 1,4-configuration in the copolymer is statistical, their content determines the average molecular weight of the degradation products (Table 7). The nature of the diene fragments in the copolymer does not affect the character of the molecular weight distribution of the PIB, which is narrower than in the initial polymer (the M_w/M_n ratio varies from 1.15 to 1.4).

Table 7. The properties of the initial copolymers and the products of their oxidative degradation. [71]

Initial copolymer				Functional PIB derivative	
$10^{-4}\cdot\bar{M}_v$	$\bar{M}_w/\bar{M}_n$	content of diene, mole %	F, wt.%	$\bar{M}_n$	f
Isoprene					
60	—	1.2	20.6	4800	0.81
65	1.8	1.2	20.6	4150	0.9
40	2.84	2.2	17.6	2500	0.92
53	—	6.3	10.3	1080	0.95
Penta-1,3-diene					
38	—	2.3	10.0	2400*	0.97*
38	—	2.3	10.0	2350	1.85
40	—	1.8	—	3500	1.88
35	—	3.6	12.0	1700	1.9
45	2.54	2.0	—	2900*	0.95*
45	2.54	2.0	—	2900	1.9

Notation: $\bar{M}_v$ is the viscosity-average molecular weight, $\bar{M}_w/\bar{M}_n$ the width of the molecular weight distribution, F the content of vinyl units relative to the total number of C=C bonds, and f the functionality with respect to the carboxy-group [number of carboxy-groups per unit].
*Obtained on ozonolysis in the presence of pyridine.

The functionality with respect to the carboxy-group [the number of carboxy-groups per unit] varies from 0.81 to 1.9 as a function of the conditions in the synthesis and the products contain mono-, bi-, and poly-functional derivatives of PIB (Table 8). The presence of "anomalous" fractions with a **functionality** in excess of one (in the case of a ketoacid) or more than two (in the case of a dicarboxylic acid) is due to the deviations from the 1,4-structure of the copolymer [71] in the course of the cationic copolymerisation of the diene with IB. The presence of diene units with 1,2- and 3,4-configurations in the copolymer (Table 7) leads to the formation of formaldehyde and formic acid in the ozonolysis products in accordance with Scheme 16:

Scheme 16

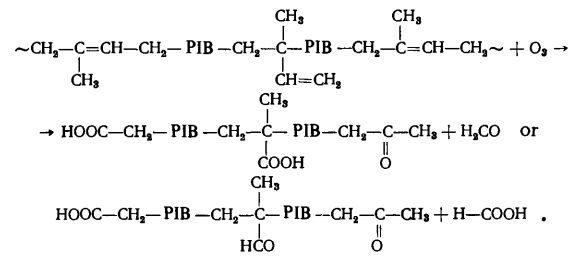


Table 8. Characteristics of carboxyl-containing PIB. [71]

Functional PIB derivative	$\bar{M}_n$	Content of fractions (wt.%) for different functionalities					
		0	1	>1	2	2*	>2
HOOC—PIB —C(=O)—CH$_3$	4800	12.48	70.0	17.5	—	—	—
HOOC—PIB —C(=O)—CH$_3$	2300	6.23	70.63	—	5.87	17.25	—
HOOC—PIB —COOH	2300	6.23	18.3	—	70.85	—	4.62

*Relative to aldehyde groups.

Thus the nature and the number of functional groups in the PIB obtained by the oxidative degradation of the products of the cationic polymerisation and copolymerisation of IB depend to a large extent on the composition and structure of the initial polymers. The development of this method of synthesis of functional derivatives of PIB is therefore associated with the improvement of procedures for the regulation of both the oxidative degradation and copolymerisation processes.

IV. REACTIONS OF ISOBUTENE POLYMERS VIA END GROUPS

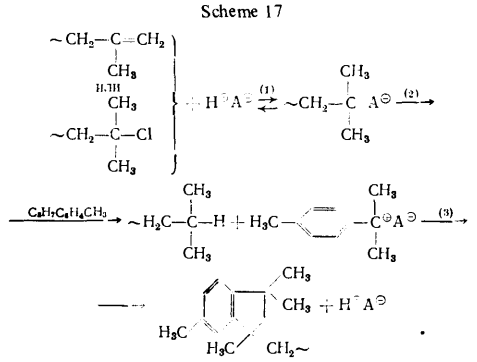
The PIB with one or two reactive end groups obtained in polymerisation or degradation processes are modified by polymer-analogue transformations in order to obtain other functional PIB derivatives (Table 9). These reactions are carried out under conditions which rule out the decomposition and cross-linking of the PIB macrochains. The presence of even one C=C terminal bond in low-molecular-weight PIB makes it possible to introduce into the polymer various groups (chlorine, aromatic groups, etc.).

In contrast to IB, which combines quantitatively with HCl, PIB with a molecular weight of 800 is only partially hydrochlorinated (in solution in toluene the degree of conversion of PIB after 3 h is not more than 50% at 0 °C), while in aliphatic solvents it is totally inactive. [75] With increase in solvent polarity or in the presence of weak Lewis acids ($FeCl_3$, $SnCl_4$, etc.) the degree of conversion of PIB with respect to the end group increases to 86%.

The alkylation of aromatic hydrocarbons (benzene, toluene, [64] and phenol) by PIB with terminal C=C and C–Cl bonds on treatment with acid catalysts leads to the formation of aromatic polyisobutene compounds. In the case of 1-isopropyl-4-methylbenzene, ionic hdyrogenation of PIB takes place under these conditions [77] in accordance with Scheme 17,

which involves the formation of a macrocation [reaction (1)], hydride transfer [reaction (2)], and cycloalkylation of the aromatic ring attached to the second generation carbonium ion [reaction (3)]:

Scheme 17



In contrast to catalytic hydrogenation by molecular hydrogen under severe conditions,[78] the ionic hydrogenation reaction takes place at room temperature without high pressure and leads to the formation of PIB with isobutyl and indan groups at the end of the chain in equimolar proportions. The presence of the latter in the products has been demonstrated by ultraviolet spectroscopy and model reactions of di-isobutylene.[79]

The high-molecular-weight alkenylsuccinic anhydride has been obtained in yields up to 58% by the condensation of an unsaturated PIB (molecular weight 800–1000) with maleic anhydride (230 °C, 10 h).[80] Reactions involving hydrosilylation with trichlorosilane and alkylchlorosilanes in the presence of the H_2PtCl_6 catalyst with formation of Si–Cl and (on reduction) Si–H groups are of interest.[51] Various sulphur-containing PIB derivatives can be obtained by the addition of sulphur dichloride, 4-chloro-5-chlorosulphenyl-3-methyltetrahydrophthalic anhydride, or 9-chloro-10-chlorosulphenylstearic acid.[82] PIB chlorination, sulphonation, oxidation, and epoxidation reactions, accompanied not only by the modification of the terminal C=C bonds but also by a change in the chemical nature of the chain are likewise known.[1] Analogous reactions can evidently be achieved with αω-divinyl-PIB obtained by the dehydrochlorination of αω-dichloro-PIB in the presence of $t\text{-}C_4H_9OK$.[83] It has been shown[84] that the epoxidation of PIB containing the vinyl C=C bonds at the end of the chain with the aid of *m*-ClC_6H_4COOOH and subsequent treatment with $ZnBr_2$ lead to a polymeric dialdehyde.

An important intermediate in the synthesis of functional PIB is a carboxyl-containing polymer obtained in the oxidative degradation of PIBC containing dienes[74] or on oxidation in the presence of RuO_4 of PIB with aromatic fragments at the ends of the chain.[86] When αω-dicarboxy-PIB is treated with thionyl chloride, it is readily converted into the corresponding bifunctional acid chloride.[74,86] PIB with carboxy-acid chloride groups have been used for the synthesis of low-molecular-weight polymers with hydroxy-, phenolic, phosphorus-containing, amine, and amidoamine reactive end groups (Table 9). A method of synthesis of dihydroxy-PIB by the hydroboration of αω-divinyl-PIB with subsequent oxidation in an alkaline medium has been described.[85] The product reacts further with isocyanates,[85,89] chlorosilanes,[85] and other reagents. This extends the series of functional PIB. However, one should note that the use of methods for introducing functional groups into high-molecular-weight PIB obtained beforehand is sometimes restricted by the decrease in the reactivity of the end groups with increasing molecular weight of the polymer[79,90] or by the decomposition of the polymer chain under the reaction conditions.[64] These features distinguish the reactions of PIB involving end groups from the reactions of its low-molecular-weight analogues.

Table 9. Modification of PIB via end groups.

Initial groups in PIB*	Reagents	Groups in modified PIB	Refs.
$t\text{-}C_4H_9\sim CH_2\text{—}C(CH_3)=CH_2$	HCl (cat.) C_6H_5R (cat.) H_2 (cat.)	$t\text{-}C_4H_9\sim C(CH_3)_2Cl$ $t\text{-}C_4H_9\sim C_6H_4R$ $t\text{-}C_4H_9\sim CH_2CH(CH_3)_2$	[75] [64,76,77] [78–79]
		$t\text{-}C_4H_9\sim CH{=}CCH_3$ (indan)	[80]
	$HSiCl_3$	$t\text{-}C_4H_9\sim SiCl_2CH_3$	[81]
	RSCl	$t\text{-}C_4H_9\sim CH_2C(CH_3)_2SR$ Cl	[82]
$ClC(CH_3)_2\sim CH_2C(CH_3)_2Cl$	$t\text{-}C_4H_9OK$	$CH_2{=}C(CH_3)\sim CH_2C(CH_3)_2Cl$ CH_3 CH	[83]
$ClCH_2C(CH_3)_2\sim CH_2\text{—}$ $\text{—}C(CH_3)_2Cl$	MeOH	$ClCH_2C(CH_3)_2\sim CH_2C(CH_3)_2OCH_3$	[84]
$CH_2{=}C(CH_3)\sim CH_2C(CH_3){=}CH_2$	*m*-$Cl\text{—}C_6H_4CO_3H$	O $CH_2C(CH_3)_2\sim CH_2CH(CH_3)CH_2$	[84]
	BH_3; O_2(NaOH)	$HOCH_2CH(CH_3)CH_2\sim CH_2CH(CH_3)CH_2OH$	[85]
$t\text{-}C_4H_9\sim C_6H_4R$	RuO_4	$t\text{-}C_4H_9\sim COOH$	[86]
$RC_6H_4\sim C_6H_4R$	RuO_4	$HOOC\sim COOH$	[86]
$HOOC\sim COOH$	$SOCl_2$	$ClOC\sim COCl$	[74,86]
	$LiAlH_4$	$HOCH_2\sim CH_2OH$	[74]
	HOROH	$HOROC(O)\sim C(O)OROH$	[74]
	H_2NRNH_2	$H_2NRNHC(O)\sim\sim C(O)NHRNH_2$	[87]
	$CH_2\text{—}CH\text{—}R$ O	$HOCH_2CHOC(O)\sim$ R $\sim C(O)OCHCH_2OH$ R	[74]
$ClC(O)\sim C(O)Cl$	S	S	
	$HS\text{—}P(OR)_2$	$(RO)_2P\cdot C(O)\sim$ S $\sim C(O)\cdot P(RO)_2$	[88]
	ROH	$ROC(O)\sim C(O)OR$	[88]
$HOCH_2\sim CH_2OH$	HOROH	$HOROC(O)\sim C(O)OROH$	[88]
	$ClSi(CH_3)_3$	$(CH_3)_3SiOCH_2\sim\sim CH_2OSi(CH_3)_3$	[85]
	C_6H_5NCO	$C_6H_5NHC(O)O\sim\sim OC(O)NHC_6H_5$	[85]
	ClC(O)NCO	$OCNCOO\sim OCONCO$	[89]
$CH_2\text{—}C(O)\text{—}CH_2\sim CH_2C(O)\text{—}CH_2$ CH_3 CH_3	$ZnBr_2$	$OCH\text{—}CH\text{—}CH_2\sim$ CH_3 $\sim CH_2\text{—}CH\text{—}CHO$ CH_3	[84]

*The symbol ~ denotes $-[CH_2\text{—}C(CH_3)_2\text{—}]_n$.

V. APPLICATIONS OF THE FUNCTIONAL DERIVATIVES OF ISOBUTENE POLYMERS

The employment of functional derivatives of PIB in the traditional applications of PIB which have a single double bond at the end of the chain (electrically insulating oils, components of inorganic and synthetic oils, additives to such oils, cooling and lubricating liquids, and ingredients of compound preparations for different purposes[1,91,92]) is of great practical interest. This is because the introduction of functional groups into PIB by the methods described above results in a significant improvement of certain useful properties of the polymer. For example, low-molecular-weight PIB containing heteroatomic fragments at the ends of the chain are characterised by an increased resistance to oxidation compared with unsaturated PIB (octol) (Table 10).

Table 10. Oxidation of functional derivatives of low-molecular-weight PIB at 200 °C and an O_2 pressure of 250 mmHg.[74]

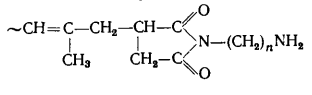
End groups in PIB	Inductive period in oxidation reaction, min
t-C_4H_9~, ~$C(CH_3)=CH_2$, ~$HC=C(CH_3)_2$	0
~COOH, ~$C(O)CH_3$	10
~OH	35
~NH_2	45
~$C(O)SP(O)(OR)_2$	55
~C_6H_4OH	135

The products of the hydrogenation of PIB [79] and aromatic polyisobutene compounds[22,93] exhibit a high resistance to mechano- and thermo-oxidative degradation. The presence of phenolic fragments in the functional PIB derivatives imparts to them the properties of antioxidants.[22]

PIB with terminal carbonyl and carboxy-groups, used as viscosity controlling additives to oils, show a greater thickening capacity than their unsaturated analogues. Functional derivatives of PIB increase the viscosity index without influencing the setting temperature of the petroleum oil and improve its thermal and mechanical stability.[94]

Polyisobutylene with phosphorodithioate end groups (1.5 wt.% of phosphorus and 2.7 wt.% of sulphur) show a polyfunctional activity in lubricating oils, exhibiting not only thickening but also antioxidant, antitear, and antiwear properties. Additives of this type can be regarded as essential materials for creating lubricating oil compositions with improved properties and with a reduced number of components. The high thermo-oxidative stability of these polymers is associated with the formation of phosphorodithioate radicals, which inhibit the decomposition of PIB.[88]

Ashless additives, which are the products of the interaction of polyisobutylenesuccinic anhydride with amines, i.e.



have found extensive applications. A characteristic feature of succinimide additives to motor oils is their effective detergent and dispersing action.[95]

The employment of PIB with carboxy- and keto-end groups as plasticising additives to rubbers makes it possible to improve the frost resistance and the physicomechanical properties of vulcanised chloroprene rubber.[96]

Oils based on aromatic polyisobutylene compounds are distinguished by a low setting temperature.[20] Saturated PIB are also used as lubricating materials in various branches of industry, medicine, and cosmetics.[78]

An advantage of hydrogenated PIB is that, when they are employed as dielectric fluids, the useful life of condensers is 3–4 times longer than in the case where octol (unsaturated PIB) is used as the condenser oil.[79]

High-molecular-weight PIB has a high chemical stability and resistance to ageing but is inadequately compatible with inorganic fillers. Since polymers are used in mixtures with fillers in techniques designed to protect against corrosion and to ensure hermetic seals,[92] the presence of functional groups in PIB is important for the improvement of the compatibility of the mixture components. Functional derivatives of PIB are of greatest interest for the preparation of various gasket and film materials and also compound mixtures, hermetic seals, non-drying putty, adhesive tapes, greases, and dyes, among other general purpose technical materials. By altering the polarity of the macromolecules as a result of the introduction of functional end groups into PIB, it is apparently possible to eliminate also the disadvantage of polyisobutene hermetic seals such as low cohesive strength and instability in relation to oils, fats, lubricants, and many solvents.[92]

Examples of the effective employment of PIB with carboxylic end groups for the modification of polymeric composites based on the acrylonitrile-butadiene-styrene copolymer, which are produced industrially, have been described.[97]

Apart from the traditional applications of PIB, the synthesis of their functional derivatives gives rise to prospects for the creation of liquid rubbers of a new type.[2] The combination of the saturation of the isobutene chain, which imparts a high chemical stability, impermeability to gases, and compatibility with certain polymers to articles based on high-molecular-weight polymers with the advantages arising from the ease of working with liquid rubbers containing highly reactive groups should ensure a wide variety of applications of these compounds. The hardening of oligoisobutenedicarboxylic acid by epoxy-compounds in the presence of tertiary amines as catalysts is accompanied by the formation of rubbers with a regular three-dimensional network.[90]

The presence of the reactive acid chloride group in PIB permits the subsequent grafting of starch via the CH_2OH groups[98] and also the preparation of a PIB block copolymer with polystyrene by reaction with the "living" polymer.[86]

Depending on the number and nature of the reactive groups, functional derivatives of PIB can be used as prepolymers in the synthesis of block copolymer of the type PIB-A, A-PIB-A, and $(PIB)_nA_m$, where A are blocks of a polymer differing in its nature from PIB. For example, the diblock (PIB–PST) and triblock (PST–PIB–PST) copolymers have been obtained by initiating the cationic polymerisation of styrene with alkyl derivatives under the influence of the PIB-Cl + alkylaluminium halide macromolecular initiator.[99]

Monofunctional PIB with a terminal chlorine atom attached to a teritary carbon atom reacts to form an IB block copolymer with styrene having a molecular weight up to 80000–100000 with a conversion up to 98% after the addition of $Al(C_2H_5)_2Cl$ and styrene.[100] Functional derivatives of diblock copolymers of isobutene with styrene or α-methylstyrene have been synthesised by an analogous procedure. PIB with a molecular weight from 9300 to 14300, having a tertiary Cl atom at one end of the chain and the $(CH_3)_2C=CH-CH_2$~ or $CH_2=CH-C(CH_3)_2$~ group at the other, was used as the prepolymer.[37] It has been shown[101] that chain transfer to α-methylstyrene with formation of a homopolymer does not occur in this instance and the product is characterised by a unimodal molecular weight distribution.

The reaction of bifunctional PIB having terminal chlorine atoms (whose molecular weights are in the range 30000–100000) with α-methylstyrene in the presence of $(C_2H_5)_2AlCl$ leads to a triblock copolymer consisting of a central PIB block and two terminal poly-α-methylstyrene blocks.[48]

The polymeric Grignard reagent synthesised on the basis of αω-dichloro-PIB has been used to prepare a new poly(isobutene–block–methyl methacrylate) block copolymer[43] in accordance with the scheme

Scheme 18

$$\mathrm{ClCH_2{-}C(CH_3)_2{-}PIB{-}CH_2{-}C(CH_3)_2Cl} \xrightarrow[2)\ Mg\ (THF)]{1)\ CH_3OH(HCl)} \longrightarrow$$
$$\longrightarrow \mathrm{ClMg{-}CH_2{-}C(CH_3)_2{-}PIB{-}CH_2{-}C(CH_3){=}CH_2} \xrightarrow{MMA} \longrightarrow$$
$$\longrightarrow \sim\mathrm{PMMA{-}CH_2{-}C(CH_3)_2{-}PIB{-}CH_2{-}C(CH_3)_2{=}CH_2}\ ,$$

where MMA is methyl methacrylate and PMMA is poly(methyl methacrylate).

By virtue of the presence of polystyrene, poly-α-methylstyrene, poly(methyl methacrylate), and other blocks in the products, they have the properties of thermoelastoplastics.[43] This leads to promising new applications of isobutene polymers.

The methods for the introduction of functional end groups into PIB reflects the characteristic features of the synthesis and properties of the polymer. The inapplicability to PIB of the method for the introduction of functional groups traditional for polymers based on anion-active monomers and based on the principle of "living polymerisation" as well as the limited possibility for polymer-analogue transformations via the terminal double bond have given rise to the use of new procedures. These include the cationic polymerisation of IB, regulated at the level of elementary chain intitiation and termination (transfer) stages, using specially selected complex catalysts, weak electron-donating compounds (chain transfer agents), proton traps, etc., which makes it possible to synthesise PIB with specified functional groups at the end of the chain. The picturesque term "molecular engineering" given to this method for the introduction of functional groups into PIB [102] neatly reflects the high level of the solution of the problem: together with the specified functionality and the distribution of functional groups, a specific molecular weight, molecular weight distribution, and microstructure of the polymer are ensured. In other words, one is dealing with the synthesis of functional derivatives of PIB regulated at different levels.

By means of further development of research into the controlled cationic polymerisation of IB in the absence of protic initiation and chain transfer to the monomer, it is possible to approach and even surpass the synthetic possibilities of "living" systems as regards the preparation of a wide variety of block and grafted copolymers.[102]

The synthesis of cationic copolymers (susceptible to regulation) of IB with diene (1,4-addition) and triene (1,6-addition) monomers and subsequent oxidative degradation under specially selected conditions also lead to extensive possibilities for the synthesis of functional PIB derivatives. Despite the large number of stages involved and their complexity, the oxidative degradation methods can compete successfully with polymerisation procedures for the synthesis of functional PIB derivatives, particularly in the synthesis of high-molecular-weight dihydric alcohols and dicarboxylic acids. The range of chemical reactions and applications of PIB as hermetic seals, oils, additives, etc. can be significantly extended by modifying the polymer at the end groups. The presence of reactive groups in functional PIB derivatives makes it possible to combine this polymer chemically with "incompatible" plastics and elastomers to form polymeric products with a unique set of properties.

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Paramagnetic d^1-Complexes of Biscyclopentadienylvanadium

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Electron paramagnetic resonance data for the Cp_2V d^1-complexes are surveyed and the dependence of the EPR parameters for the complexes on their molecular and electronic structure is discussed. Examples of the use of the EPR method for the determination of the structures of labile Cp_2V d^1-complexes, formed as intermediates in various reactions, are considered. The bibliography includes 59 references.

CONTENTS

I. Introduction 724
II. The EPR spectra of Cp_2V d^1-complexes 724
III. The EPR parameters and structure of Cp_2V d^1-complexes 728
IV. EPR study of Cp_2V d^1-complexes in solution 732

I. INTRODUCTION

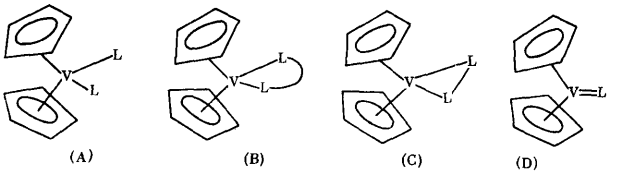
The electron paramagnetic resonance method is widely used for the solution of various problems in the chemistry of organometallic compounds (OMC), including the determination of their molecular and electronic structures. We believe that this aspect of the application of the EPR method to the OMC chemistry is most important and interesting. Unfortunately, the EPR study of paramagnetic OMC is frequently undertaken with the utilitarian aim of obtaining the spectroscopic characteristics of the given specific compounds. For this reason, most of the available EPR information obtained in OMC chemistry is concerned with specific species, is of an unrelated character, and is relatively unsuitable for the solution of problems involving the determination of the electronic and molecular structures of OMC because success in research of this kind is impossible without the elucidation of the influence of the ligand environment on the EPR parameters.

In the present review an attempt is made to survey EPR data obtained for the Cp_2V d^1-complexes: the spectroscopic parameters are compared with the available information about the molecular and electronic structures of these complexes; certain rules governing the variation of the EPR parameters as a function of the nature of additional ligands attached to Cp_2V are discussed; the relations found between the EPR parameters and the structure are used to determine the structures of labile Cp_2V d^1-complexes formed as intermediates in various reactions involving Cp_2V and its derivatives.

II. THE EPR SPECTRA OF Cp_2V d^1-COMPLEXES

1. Types of Cp_2V d^1-Complexes. General Information about the Molecular and Electronic Structures

A paramagnetic 17-electron vanadium d^1-complex incorporating Cp_2V can be formally produced from the 15-electron complex Cp_2V by adding to the latter either two one-electron ligands or one two-electron ligand. The first variant can be achieved in only one way—as a result of the formation of two σ-bonds between Cp_2V and two one-electron ligands (A).



(A) (B) (C) (D)

Depending on their nature (structure), the two-electron ligand can be linked to vanadium in three different ways. Bidentate chelate ligands (formally η^2-ligands), in which the atoms bound directly to vanadium are not linked to one another, form complexes of type (B) which differ little from complexes of type (A) (in terms of the character of the V–L bond) and can be regarded as d^1-complexes with two one-electron η^1-ligands. Bidentate ligands in which the atoms bound to vanadium are linked directly to one another form on addition to Cp_2V a three-membered metallocycle. In the resulting d^1-complex a two-electron η^2-ligand (C) is bound to Cp_2V. The third "terminal" type of binding of the two-electron ligand to Cp_2V leads to d^1-complexes with a two-electron η^1-ligand (D).

The majority of the known Cp_2V d^1-complexes belong to the first two types [(A) and (B)]. The one-electron η^1-ligand which enters into the composition of type (A) complexes can be of a wide variety of types: the halogens (Cl, Br, and I), the pseudohalogens (CN, OCN, SCN, SeCN, and N_3), carboxy-compounds (OCOPh), alkyls (Me, Et, CH_2Ph, and CH_2SiMe_3), hydrogen, element-containing groups (SiR_3, GeR_3, SnR_3, and SR), etc. The complex can contain both two identical and two different additional ligands. In complexes of type (B) the ligands bound to vanadium may be various chelate species forming four-, five-, and six-membered rings; their coordinating atoms may be C, O, N, and S.

The two-electron ligands in the main react with Cp_2V to form complexes of type (C) (η^2-ligands). A fairly large number of such complexes are known in which the ligands are alkenes EtOC(O)C(H) = C(H)C(O)OEt, F_3CFC = $CFCF_3$), alkynes (PhC≡CPh, $C_6F_5C{\equiv}CC_6F_5$, etc.), diazenes (PhN=NPh), heterocumulenes ($Ph_2C{=}C{=}O$, Ph–N=C=O, S=C=S). Among complexes of type (D) described in the literature, one may refer to compounds with carbon monoxide, isonitriles, and nitrenes.

The classification of complexes of type (C) and (D) as d^1-complexes still remains controversial. Thus the authors of a review[1] regard Cp_2V complexes with ligands of this kind as d^3-complexes, assuming that the ligands in them are neutral and that the formal oxidation state of vanadium in the complexes is +2. This view has been confirmed by the results of quantum-chemical calculations, from which it follows that the highest fully occupied molecular orbital in the complexes involves a large contribution by the d orbitals of the atom.[2] On the other hand, the results of calculations indicate an appreciable decrease of the energy of this orbital compared with the initial d^3-complex (Cp_2V), i.e. the transformation of this orbital from non-bonding to bonding. The available data concerning the molecular structure of certain d^1-complexes with η^2-ligands[3-5] also show that the alkene and alkyne molecules coordinated to Cp_2V undergo appreciable deformations, the resulting structures approaching those of alkanes and alkenes respectively. The V–C bond lengths in these complexes are comparable to those of the normal V–C σ-bonds. Thus the binding of vanadium to the carbon atoms in the complexes of type (C) differs little in its character from the σ-binding in complexes of types (A) and (B). In order to compare the properties of different 17-electron Cp_2V complexes, in the present review compounds of types (C) and (D) will be considered together with those of types (A) and (B) and will be classified as d^1-complexes.

The general features of the molecular and electronic structures of the Cp_2V d^1-complexes are well known. Admittedly, this claim refers to a large extent to complexes of type (A) (with two one-electron ligands), for which fairly reliable quantum-chemical calculations have been performed,[6,7] whose results agree well with EPR experimental data for diamagnetically diluted single crystals.[8,9] As regards complexes of the other three types, their electronic structures can be inferred on the basis of a qualitative "angular sandwich" structural model[2] and also on the basis of the available data for the molecular structure of such complexes. Here one should naturally take into account the similarities and differences in the structures of complexes of different types and the character of the bond linking the additional ligand to Cp_2V.

In conformity with the available data, the general features of the structure of Cp_2V d^1-complexes are as follows. Their molecular geometry is described in an idealised manner by C_{2v} symmetry with a twofold symmetry axis, which coincides with the X axis (for the arrangement of the coordinate axes illustrated in Fig.1). In the presence of different additional ligands, the symmetry of the complex decreases to C_2.[2] For the arrangement of coordinate axes shown in Fig.1, the lines joining vanadium to the centres of the Cp ligands are in the xy plane and the bonding to the additional ligands L is in the xz plane. In this case the unpaired electron is located in the molecular orbital with a_1 symmetry. In terms of its character, this orbital is non-bonding with a dominant contribution from the d_{z^2} orbital of vanadium. Taking into account the ligand contribution, the expression for the molecular orbital of the electron (MO_e) can be formulated as follows:

$$\varphi^e_{a_1} = \alpha(d_{z^2},\ d_{x^2-y^2}) + (1-\alpha)^{1/2}\varphi_L, \qquad (1)$$

where α and $(1-\alpha)^{1/2}$ are the coefficients of the orbitals forming part of the composition of MO_e and ϕ_L is the combined orbital of the ligands with a^1 symmetry.

According to the results of quantum-chemical calculations,[6,7] the contribution of the vanadium orbitals (d orbitals) is from 58 to 72% depending on the nature of the additional ligands, the contribution of the ligand orbitals (p_π orbitals) is 23–37%, and the contribution of the orbitals of the Cp ligand does not exceed 5%. It is striking that MO_e contains virtually no contribution from the s orbitals of the ligands (< 1%). An interesting feature of the Cp_2V d^1-complexes is the dependence of the relative contributions of the d_{z^2} and $d_{x^2-y^2}$ orbitals of vanadium on the nature of the additional ligands. This dependence is manifested very distinctly in the anisotropic EPR spectra and will be discussed in detail when such spectra are considered.

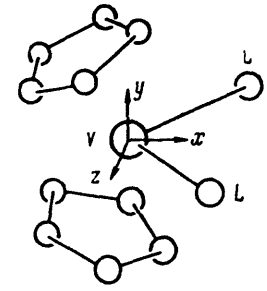


Figure 1. The molecular geometry and disposition of the coordinate axes in Cp_2V d^1-complexes.[20]

Table 1. Parameters of the isotropic EPR spectra of Cp_2V d^1-complexes.

No.	Complex	g_i	$-A(^{51}V)$, G	Refs.
1	Cp_2VCl_2	1.9876	74.2	[9]
	Cp_2VCl_2	1.9880	74.3	[10]
2	Cp_2VBr_2	1.999	67.0	[11]
	Cp_2VBr_2	2.0212	65.3	[12]
3	Cp_2VClBr	—	—	[12]
4	Cp_2VI_2	1.998	59.4	[11]
5	Cp_2VBrI	1.990	64.0	[11]
6	Cp_2VClI	1.989	66.0	[11]
7	$Cp_2V(OCN)_2$	1.985	76.1	[10]
8	$Cp_2V(NCS)_2$	1.991	73.0	[10]
	$Cp_2V(NCS)_2$	1.982	73.4	[13]
9	$Cp_2V(NCSe)_2$	1.990	73.6	[10]
	$Cp_2V(NCSe)_2$	1.981	73.0	[13]
10	$Cp_2V(N_3)_2$	1.985	72.0	[10]
11	$Cp_2V(CN)_2$	1.999	60.3	[10]
12	$Cp_2V(CN)(NCS)$	1.981	59.4	[13]
13	$Cp_2V(CN)(NCSe)$	1.983	57.5	[13]
14	$Cp_2V(NO)(Cl)$	1.993	72.0	[14]
15	$Cp_2V(NO)(Br)$	1.991	66.0	[14]
16	$Cp_2V(OCOPh)_2$	1.967	80.0	[15]
17	$Cp_2V(Me)_2$	1.9915	63.0; 4.8 (6H)	[16]
18	$Cp_2V(CH_2Me)_2$	1.995	62.4	[17]
	$Cp_2V(CH_2Me)_2$	1.9920	62.7	[16]
19	$Cp_2V(CH_2Ph)_2$	1.9910	64.0	[16]
20	$Cp_2V(CH_2SiMe_3)_2$	1.990	64.5; 3.0 (4H)	[17]
	$Cp_2V(CH_2SiMe_3)_2$	1.9916	64.3	[18]
21	$Cp_2V(Me)(CH_2SiMe_3)$	1.9926	63.7; 3.9 (3H)	[18]
22	$Cp_2V(Me)Cl$	1.9900	69.2; 3.6 (3H)	[19]
23	$Cp_2V(CH_2SiMe_3)Cl$	1.9900	70.0	[18]
24	$Cp_2V(CH_2SiMe_3)Br$	2.0223	64.5	[20]
25	$Cp_2V(SPh)_2$	2.00	62.6	[21]
26	$Cp_2V(SiEt_3)_2$	2.0047	53.4	[20]
27	$Cp_2V(GeEt_3)_2$	2.0025	55.2	[22]
28	$Cp_2(SnEt_3)_2$	2.0032	50.7; 154 (2Sn)	[23]
29	$Cp_2V(SiCl_2Me)Cl$	1.9954	62.6	[20]
30	$Cp_2V(Cl)GeEt_3$	1.9956	66.8	[22]
31	$Cp_2V(Br)GeEt_3$	2.0167	61.7	[22]
32	$Cp_2V(Cl)Ge(C_6F_5)_3$	1.9936	64.7	[24]
33	$Cp_2V(CH_2Me)Ge(C_6F_5)_3$	1.9936	60.0	[24]
34	$Cp_2V(Cl)Ge(C_6F_5)_2H$	1.9946	64.4	[20]
35	$Cp_2V(H)SnEt_3$	2.0007	41.6; 14.6 (1H); 143 (1Sn)	[23]
36	$Cp_2V(Cl)SnEt_3$	1.9946	62.0; 188 (1Sn)	[23]
37	$Cp_2V(Br)SnEt_3$	2.0170	61.5; 145 (1Sn)	[23]
38	$Cp_2V(CH_2Me)SnEt_3$	1.9964	60.8; 143 (1Sn)	[23]
39	$Cp_2V(CH_2SiMe_3)SnEt_3$	1.9964	60.8; 5.2 (2H); 143 (1Sn)	[23]
40	$Cp_2VGe(C_6F_5)_3HgGe(C_6F_5)_3$	1.978	52.6; 116 (1Hg)	[24]
41	Cp_2VS_5	2.00	61.4	[25]
	Cp_2VS_5	—	64.8	[8]

Table 1. (continued)

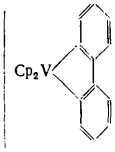
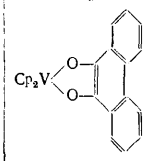
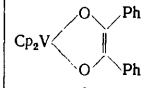
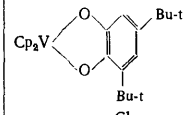
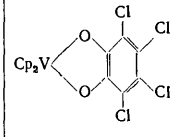
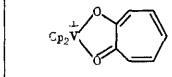
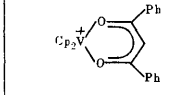
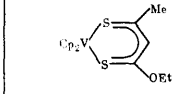
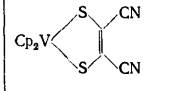
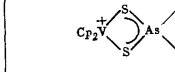
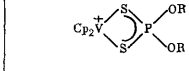
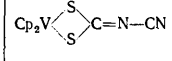
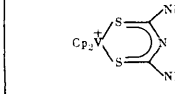
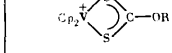
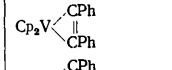
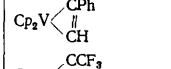
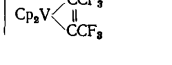
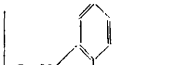
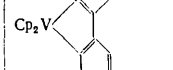
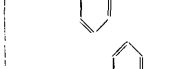
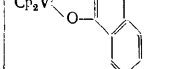
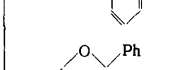
No.	Complex	g_i	$-A(^{51}V)$, G	Refs.
42		2.00	47	[26]
43		1.9795	70.0	[27]
44		1.9760	71.7	[27]
45		1.9797	70.2	[28]
46		1.9812	68.9	[28]
47		1.983	65.9	[10]
48		1.985	74.6	[10]
49		1.982	60.5	[29]
50		1.985	59.4	[29]
51		1.985	65.7; 40.3 (1As)	[29]
52		1.98	63.6; 44.5 (1P)	[30]
53		1.990	60.5	[29]
54		1.990	60.5	[29]
55	 R = Me, Et, Pr, iso-Pr, cyclo-C_6H_{11}	1.985—1.990	60.5—62.5	[31]
56		1.9968 1.9970	43.1 42.6	[5] [28]
57		1.9968 1.9966	44.8 42.9	[5] [28]
58		1.9968 1.9971	44.6 46.0	[5] [52]

Table 1. (continued)

No.	Complex	g_i	$-A(^{51}V)$, G	Refs.
59		1.9983	44.6	[3]
60		1.9976 1.9968	44.0 43.3	[32] [5]
61		1.9968	45.0	[5]
62		1.9968 1.9970	45.2 45.4	[5] [28]
63		2.0009	43.6	[33]
64		1.9976	45.5	[34]
65		1.9961	43.7	[28]
66	$Cp_2V[N_2C(HC(O)OEt)_2]$	1.9942	41	[35]
67	$Cp_2V(N_2CPh_2)$	1.9918	23	[35]
68		1.9953	41	[35]
69	Cp_2VCO	2.0015	27.7	[28]
70	Cp_2V (CN-t-Bu)	2.0022	27.0	[20]
71	Cp_2V (CN-cyclo-C_6H_{11})	2.0019	27.3	[20]

2. Isotropic EPR Spectra of Cp_2V d^1-Complexes

The isotropic parameters of the EPR spectra of d^1-complexes of various types are presented in Table 1. The data in this table show that, depending on the nature of the additional ligands bound to vanadium, the isotropic parameters vary within wide limits. The constants for the hyperfine interaction with the ^{51}V nucleus (99.9%; $J = 7/2$; $\mu = 5.1392$) $A_i(V)$ vary from -23 to -80 G and the g_i range from 1.965 to 2.025. Comparative analysis of the isotropic parameters of the spectra of the Cp_2V d^1-complexes makes it possible to discover certain relations governing their variation as a function of the properties of the additional ligand. These relations are clearly illustrated by the "field" of the values of g_i and $A_i(^{51}V)$ in which the majority of the known Cp_2V d^1-complexes are represented (Fig.2).

Virtually all d^1-complexes of type (A) (two one-electron ligands) fit on a straight line (linear correlation between g_i and A_i), constituting one group. An analogous relation has been observed for d^1-complexes of type (B) (chelating two-electron ligands); the straight line combining these complexes has approximately the same slope but differs in the linear term. For complexes of type (C) (two-electron η^2-ligand), the hyperfine interaction constant A_i varies very slightly with L, remaining virtually invariant. An analogous tendency has been noted for complexes of type (D) (two-electron η^1-ligand), but the number of examples of complexes of this type is small. Cp_2V complexes with carbon-containing additional ligands, in which the coordination is via carbon atoms [dialkyl derivatives of type (A), alkene and alkyne complexes of type (C), and carbonyl and isonitrile complexes of type (D)] constitute yet another group of d^1-complexes with its own linear relation between the isotropic parameters.

The groups enumerated include almost all Cp_2V d^1-complexes for which the parameters of the isotropic EPR spectra are known.

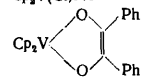
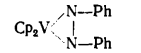
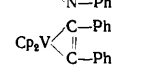
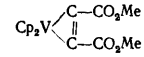
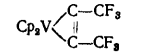
It is striking that the composition of the groups combining complexes in terms of the isotropic parameters of the EPR spectra is consistent with the formal types of these complexes based on the nature of the binding of the additional ligands to Cp_2V (see Section I). This indicates, on the one hand, the similarity of the molecular and electronic structures of isotypical complexes within each group and, on the other hand, differences between the complexes in different groups (different types). The correlation between the parameters of the carbon-containing d^1-complexes of different types emphasises common features in the electronic structures of all the Cp_2V d^1-complexes. The relation between the spectroscopic parameters and molecular electronic structures of Cp_2V d^1-complexes appears most distinctly in the analysis of anisotropic EPR spectra.

3. Anisotropic EPR Spectra of Cp_2V d^1-Complexes

Anisotropic EPR spectra have been investigated for a much smaller number of Cp_2V d^1-complexes than the isotropic spectra although the information obtained from the analysis of the former makes it possible to understand certain important details of the electronic and molecular structures of these complexes (the composition of the molecular orbital of the unpaired electron, the relative energy of the lowest occupied and unoccupied MO, and the geometry of the complex). Table 2 presents anisotropic EPR spectroscopic parameters of Cp_2V d^1-complexes. The majority of the data quoted were found in the study of "vitrified" solutions and only the data concerning Cp_2VCl_2 and Cp_2VS_5 have been obtained in experiments with diamagnetically diluted single crystals.[8,9]

It follows from Table 2 that the $\bar{g}$ and $\bar{T}$ tensors for all the d^1-complexes have orthorhombic symmetry (the principal components of the $\bar{g}$ and $\bar{T}$ tensors are not the same). The anisotropic EPR spectra of the series of Cp_2V d^1-complexes were interpreted incorrectly in a number of studies[29,31,36] based on the hypothesis of axial symmetry of the $\bar{g}$ and $\bar{T}$ tensors, the authors failing to take into account the z components of the two tensors.

Table 2. Parameters of the anisotropic EPR spectra of Cp_2V d^1-complexes.

Complex	g_x	g_y	g_z	T_x, G	T_y, G	T_z, G	Refs.
Cp_2VCl_2	—	—	—	—80.1	—127.2	—28.6	[37]
Cp_2VCl_2	1.986	1.971	2.000	—79.2	—125.2	—16.3	[6]
$(C_5H_4Me)_2VCl_2$	1.9802	1.9895	2.0013	—80.6	—125.5	—20.5	[9]
Cp_2VS_5	1.9964	1.9997	1.9889	—66.6	—111.3	—23.5	[8]
$Cp_2V(SCN)_2$	1.988	1.958	2.000	—76.2	—123.3	—20.5	[6]
$Cp_2V(OCN)_2$	1.985	1.957	2.000	—78.5	—127.7	—19.9	[6]
$Cp_2V(CN)_2$	1.994	1.986	2.000	—62.8	—106.0	—11.8	[6]
Cp_2VMe_2	1.986	2.005	1.984	—66	—111	—12	[28]
Cp_2VEt_2	1.977	2.000	1.993	—67.0	—108.0	—13.9	[17]
$Cp_2V(CH_2SiMe_3)_2$	1.997	1.999	1.999	—66.0	—114.5	—12.06	[17]
$Cp_2V(Cl)Me$	1.985	1.992	1.992	—73	—121	—14	[28]
	1.982	1.964	1.982	—82	—118	—15	[28]
$Cp_2V(H)SnEt_3$	1.984	2.009	2.006	—70	—58	+4	[20]
$Cp_2V(CH)(NCSe)$	1.982	1.970	2.000	—64.0	—109.8	—11.9	[13]
$Cp_2V(NCSe)_2$	1.985	1.957	2.000	—74.0	—114.6	—33.6	[13]
$Cp_2V(NCS)_2$	1.988	1.958	2.000	—75.8	—123.0	—20.4	[13]
$Cp_2V(CN)(NCS)$	1.988	1.958	2.000	—62.0	—108.2	—12.9	[13]
	1.978	2.000	1.995	—80	—64	+8	[28]
	1.9815	2.0000	2.0020	—77.5	—65.5	—2	[5]
	1.978	2.018	1.995	—80	—58	+10	[28]
	1.9815	2.0130	2.0020	—77	—58.5	—2.0	[5]
	1.9810	2.0090	2.0020	—77.5	—62.5	—2.0	[5]
$Cp_2V(CO)$	1.984	2.027	1.995	—72	—27	+16	[28]

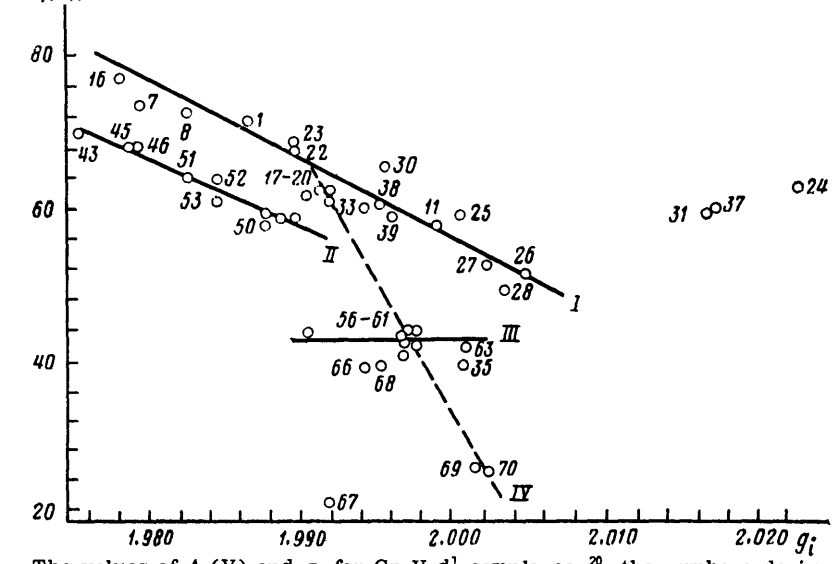


Figure 2. The values of A_i(V) and g_i for Cp_2V d^1-complexes;[20] the numbers designating the circles correspond to the numbers of the complexes in Table 1.

The interpretation of the anisotropic EPR spectra using a quantum-chemical model was first achieved for Cp_2VCl_2 in a study[37] whose authors established that the unpaired electron in Cp_2VCl_2 is located in a molecular orbital with a_1 symmetry, comprising the $3d_{z^2}$ and $3d_{x^2-y^2}$ orbitals of the metal atom. However, since the crystal structure of the matrix (Cp_2TiCl_2) was unknown at the time, it was impossible to determine the correct orientation of the axes of the $\bar{g}$ and $\bar{T}$ tensors relative to the crystal. Somewhat later a complete analysis of the anisotropic EPR spectra was carried out for a series of Cp_2V and Cp_2Nb d^1-complexes obtained in vitrified solutions.[6] Despite the fact that the initial orientation of the axes of the $\bar{g}$ and $\bar{T}$ tensors in the above investigation was selected incorrectly (the z axis coincided with the C_{2v} symmetry axis), the data obtained by the authors for the composition of the unpaired electron orbital and other details of the electronic structure differ little from the more accurate results obtained later[8,9] and based on a comparison of the parameters of the anisotropic EPR spectra of a diamagnetically diluted Cp_2VCl_2 single crystal with the quantum-chemical calculations for this complex by the Fenske–Hall method.[7] A somewhat simplified model, based on the conclusions reached in the studies listed above, as well as the investigation of Lauher and Hoffman[2] devoted to a qualitative consideration of the binding of ligands of different types in "angular sandwiches", has been used in the present review for the interpretation of the anisotropic EPR spectra of Cp_2V d^1-complexes with different ligands.

If one uses Eqn.(1) for the unpaired electron MO, then, resorting to the ligand field approximation and assuming that the contributions of the orbitals and additional ligands to the ground state are small, the principal components of the $\bar{g}$ and $\bar{T}$ tensors for the Cp_2V d^1-complexes with C_{2v} symmetry can be expressed as follows:[6,7]

$$g_x = g_0 - 2\lambda(a\cdot 3^{1/2} + b)^2\left[\frac{P^*_{b_1}}{\Delta E(\varphi^*_{b_1} \leftarrow \varphi^c_{a_1})} - \frac{1 - P^*_{b_1}}{\Delta E(\varphi^e_{a_1} \leftarrow \varphi_{b_1})}\right], \quad (2a)$$

$$g_y = g_0 - 2\lambda(a\cdot 3^{1/2} - b)^2\left[\frac{P^*_{b_2}}{\Delta E(\varphi^*_{b_2} \leftarrow \varphi^c_{a_1})} - \frac{1 - P^*_{b_2}}{\Delta E(\varphi^e_{a_1} \leftarrow \varphi_{b_2})}\right], \quad (2b)$$

$$g_z = g_0 \quad (2c)$$

$$T_x = -K + P\left[-\frac{2}{7}(a^2 - b^2) + \frac{4\cdot 3^{1/2}}{7}ab\right], \quad (3a)$$

$$T_y = -K + P\left[-\frac{2}{7}(a^2 - b^2) + \frac{4\cdot 3^{1/2}}{7}ab\right], \quad (3b)$$

$$T_z = -K + P\left[\frac{4}{7}(a^2 - b^2)\right], \quad (3c)$$

where $P = g_0 q^{51}_N \beta\beta_N \langle r^{-3}\rangle$ is the dipolar contribution, $K = -g_0 g^{51}_N \beta\beta_n \times 2/3\chi$ the contact contribution to the hyperfine interaction (HFI) with the ^{51}V nucleus, λ the spin–spin orbit coupling constant for ^{51}V, $g_0 = 2.0023$ the g-factor for the free electron, $\phi^e_{a_1}$ the molecular orbital of the unpaired electron, ϕ_{b_1} and ϕ_{b_2} are the highest fully occupied orbitals with b_1 and b_2 symmetry, $\phi^*_{b_1}$ and $\phi^*_{b_2}$ the lowest unoccupied orbitals with the same symmetries, and a and b are coefficients of the d_{z^2} and $d_{x^2-y^2}$ vanadium orbitals. The form of Eqns.(3a)–(3c) for different values of the components of the $\bar{T}$ tensor has been simplified for their more complete expression,[7] omitting small terms whose contribution to T_x, T_y, and T_z is less than 1%. On the other hand, additional terms, taking into account the spin–orbit coupling between $\phi^e_{a_1}$ and the highest fully occupied orbitals ϕ_{b_1} and ϕ_{b_2} have been introduced into the expressions for g_x and g_y, as was done by Stewart and Porte.[6] The discussion below will make clear the importance of these terms for the explanation of the values of the $\bar{g}$ tensor, especially in the case of the Cp_2V d^1-complexes with neutral η^1- and η^2-ligands.

According to Eqn.(2c), the g_z component for the Cp_2V d^1-complexes should be close to $g_0 = 2.0023$ and the T_z component should be largest, bearing in mind that all the quantities T_x, T_y, T_z, and A_i are negative. In view of these features of the z components of the $\bar{g}$ and $\bar{T}$ tensors, their assignment in the experimental spectra does not present major difficulties. The assignment of two other components, based solely on EPR spectra, is impossible, since the signs of the coefficients a and b for the metal d orbitals incorporated in $\phi^e_{a_1}$ cannot be determined from the EPR experiment. The quantum-chemical calculations[6,7] for Cp_2V d^1-complexes of types (A) and (B) yield the opposite signs for a and b, i.e. for complexes of these types $T_x > T_y$. The relative values of g_x and g_y are determined not only by the signs of the coefficients a and b but also by the relative magnitudes of the terms expressing the spin–orbital coupling of $\phi^e_{a_1}$ for the lowest unoccupied and highest fully occupied MO ($\phi^*_{b_1}$, $\phi^*_{b_2}$, ϕ_{b_1}, ϕ_{b_2}).

III. THE EPR PARAMETERS AND STRUCTURE OF Cp_2V d^1-COMPLEXES

1. Dependence of the Components of the $\bar{g}$ and $\bar{T}$ Tensors on the Structure of the Cp_2V d^1-Complexes

When use is made of the qualitative scheme proposed by Lauher and Hoffman[2] for the description of the binding of the Cp_2M fragment to the additional ligands in "angular sandwiches", then comparison of the molecular diagrams for complexes of types (A), (C), and (D) (Fig.3) can reveal significant differences, which determine the electronic structure of these complexes and hence also the parameters of the anisotropic EPR spectra.

(1) In conformity with C_{2v} molecular symmetry (with the choice of coordinate axes shown in Fig.1), the highest fully occupied MO in the complexes of all three types is an orbital with b_2 symmetry consisting mainly of contributions from the dxz orbital of vanadium and the b_2 orbital of the ligand (or ligands) and virtually lacking any contribution from the Cp ligands.

(2) The highest fully occupied and lowest unoccupied MO with b_1 symmetry consists predominantly of the d_{yz} orbital of the vanadium atom and the b_1 group orbitals of the Cp ligands and have virtually no contribution due to the orbitals of the additional ligands.

(3) In contrast to complexes of type (A), in which the b_2 orbital of the ligands is a b_2 group orbital consisting of the σ orbitals (p or s) of the ligands, in complexes of types (C) and (D) the b_2 orbital of the ligand is an antibonding orbital of a neutral ligand. As a consequence, both its energy and the energy of the b_2 orbital of the complex produced from it on formation of a bond is significantly higher than the energy of the initial σ orbitals of the one-electron ligands and the MO of the same symmetry in complexes of type (A).

The factors noted above entail two conclusions concerning the properties of the principal components of the $\bar{g}$ tensor of Cp_2V d^1-complexes. Firstly the g_x component of the $\bar{g}$ tensor must show very little sensitivity to the nature of the

additional ligands, since, as a consequence of spin–orbit coupling, the a_1 orbital of the unpaired electron becomes mixed in this instance with the MO having b_1 symmetry, which contains no contribution from the additional ligands and therefore both its energy and its composition change little when such ligands are replaced. Conversely, the g_y component must be very sensitive to changes in the properties of additional ligands, because the angular momentum operator L_y mixes the a_1 orbital of the unpaired electron with the b_2 orbital, whose energy and composition are determined by the interactions of the d_{xz} orbital of vanadium with the b_2 orbital of the ligand (or ligands). Secondly the g_y component may be greater than $g_0 = 2.0023$, since the appreciable difference between the energies of the initial b_2 orbitals of the ligands should lead to a significant difference between the energies of the MO with b_2 symmetry (ϕ_{b_2} and $\phi^*_{b_2}$) depending on the type of ligands.

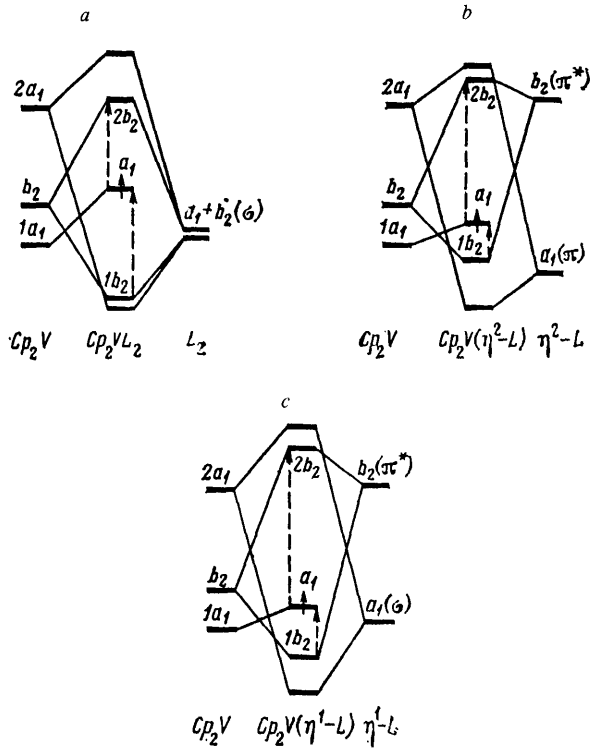


Figure 3. A qualitative energy level diagram for molecular orbitals with a_1 and b_2 symmetry in Cp_2V d^1-complexes: *a*) complexes of type (A); *b*) complexes of type (C); *c*) complexes of type (D).[20,28]

In complexes of type (A) the energy of the initial b_2 group orbital of the ligands is lower than the energy of the d_{xz} orbital of the Cp_2V complex (see Fig.3), as a result of which the energy difference ΔE between $\phi^e_{a_1}$ and ϕ_{b_2} is greater than that between $\phi^e_{a_1}$ and $\phi^*_{b_2}$, i.e. the electronic transitions predominate in the spin–orbit coupling over the "hole" transitions. Another situation arises in complexes of types (C) and (D). The high energy of the antibonding b_2 orbitals in the neutral alkene, alkyne, and CO ligands causes a shift of the energy of the b_2 and b^*_2 MO relative to the MO of the unpaired electron such that ΔE between $\phi^e_{a_1}$ and $\phi^*_{b_2}$ becomes greater than that between $\phi^e_{a_1}$ and ϕ_{b_2}, as a result of which the "hole" transitions make a greater contribution to g_y than the electronic transitions.

Unfortunately there are no literature data on the photoelectron spectra of the Cp_2V d^1-complexes of different types but such information does exist for the analogous Cp_2Mo complexes. It follows from the data of Green et al.[38] that the energy difference ΔE between the MO with a_1 symmetry, occupied in the given instance by a pair of electrons, and the orbital with b_2 symmetry (in the original study this orbital was assigned to b_1 symmetry as a result of a different type of indexing of the coordinate axes) in the complexes $Cp_2Mo(CO)$ and $Cp_2Mo(C_2H_4)$ is 0.9 eV, while in the complexes Cp_2MoMe_2 and Cp_2MoH_2 the energy differences are 2.5 and 2.2 eV respectively. At the same time, the long-wavelength transition in the electronic spectrum of Cp_2VCl_2, for example, corresponding to the excitation of the unpaired electron from the a_1 orbital to the b^*_2 orbital, is characterised by an intermediate energy of approximately 1.5 eV.[9]

On the basis of the model for binding of the additional ligands in the Cp_2V d^1-complexes considered above, the component of the $\bar{g}$ tensor greater than g_0 can be defined as the g_y component. This fact was taken into account in the compilation of Table 2, where, in contrast to the original communication,[5] the g_x and g_y components have been assigned in conformity with the model described above. Here the corresponding components of the $\bar{T}$ tensor naturally also undergo a change in indexing in such a way that $|T_x| > |T_y|$, in contrast to $|T_x| < |T_y|$ for the Cp_2V d^1-complexes of type (A). It follows from Eqns.(3a) and (3b) that the relative values of the components T_x and T_y depend only on the relative signs of the coefficients *a* and *b* defining the contribution of the vanadium d_{z^2} and $d_{x^2-y^2}$ orbitals to the MO of the unpaired electron.

Quantum-chemical calculations for the Cp_2V d^1-complexes of types (C) and (D) have not been made. As mentioned previously, calculations for the type (A) complexes lead to the conclusion that *a* and *b* have opposite signs, which is responsible for the relation $|T_x| < |T_y|$. The authors of a study[5] devoted to the analysis of the anisotropic EPR spectra of Cp_2V d^1-complexes with alkenes, alkynes, and azobenzene assume that the coefficients *a* and *b* for complexes of this type also have the opposite signs, whence follows the relation $|T_x| < |T_y|$. However, the authors[5] fail to give a correct explanation of the relation $g_x > g_y$ which follows from the preceding relation.

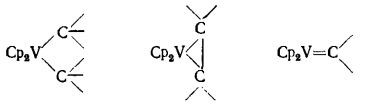
As shown above, the relation $g_y > g_0 > g_x$ between the components of the $\bar{g}$ tensor agrees best with the electronic structure of the d^1-complexes of types (C) and (D). In order to account for the relation $|T_x| > |T_y|$ associated with the above relation, one must assume that in complexes of these types the coefficients *a* and *b* have the same sign. This hypothesis agrees well with the dependence of the L–V–L valence angle on the population of the MO with a_1 symmetry known for "angular sandwiches".

The change in the relative signs of the coefficients *a* and *b* has the simple physical significance of a change in the spatial distribution of the electron density in the a_1 MO. As was correctly noted by Petersen and Dahl,[8] when $a < 0$ and $b > 0$, a small positive contribution of the $d_{x^2-y^2}$ orbital corresponds to an increase of the electron density within the L–V–L angle (along the *x* axis) and to its corresponding

decrease in the direction of the normal to the L–V–L plane (along the y axis) compared with the "pure" d_{z^2} orbital (Fig.1). The dependence of the L–M–L valence angle on the population of the MO with a_1 symmetry has been established for the Cp_2M d^0-, d^1-, and d^2-complexes: the angle L–M–L diminishes with increasing population, i.e. in this case the electronic factor (the population of the non-bonding orbital) influences the parameter of the molecular structure (the valence angle). It is natural to expect that this influence should be reciprocal, i.e. that a change in the valence angle should entail a redistribution of the spatial electron density in the a_1 MO.

It has been shown[7–9] that a simple criterion of the spatial distribution of electron density in this orbital in the transition metal d^1-complexes, especially for Cp_2V, may be the quantity a^2/b^2 determined from the anisotropic parameters of the EPR spectra. For a series of Cp_2V d^1-complexes of type (A), these quantities have been calculated.[7] Their values, which vary in the range 7.7–20, indicate the predominant contribution of the d_{z^2} orbital with a small admixture of the $d_{x^2-y^2}$ orbital. Later,[5,28] in the analysis of the EPR spectra recorded in "vitrified" toluene, it was established that the contribution of the small $d_{x^2-y^2}$ orbital for complexes of type (C) with two-electron η^2-ligands is significantly reduced ($a^2/b^2 = 70–250$), i.e. the MO of the unpaired electron is an almost pure d_{z^2} orbital.

Comparison with the available X-ray diffraction data for the structures of complexes of both types enabled the authors[5,28] to formulate a conclusion concerning the molecular structure of the complex (the L–V–L valence angle) and its electronic structure (the spatial distribution of the electron density in the a_1 MO). However for complexes of type (D) (for example, Cp_2VCO and Cp_2VCNR) a discrepancy is observed between a^2/b^2 and the L–V–L angle within the framework of this simple relation. Indeed complexes of type (D) can be regarded as limiting in the series established in accordance with a decreasing C–V–C valence angle:



(A); ~ 87° (C); 35 – 39° (D); 0°.

For complexes of type (D), in which the η-ligand is located on the x axis, the C–V–C valence angle can be regarded as zero, whence it follows that $a^2/b^2 \to \infty$, in conflict with experiment [for example, $a^2/b^2 = 13.4$ for $Cp_2V(CO)$].[28]

The conflict can be readily resolved if it is assumed that a and b have the same sign in conformity with the model of the binding of the ligands in complexes of type (C) and (D). Despite the identical values of a^2/b^2 for complexes of types (A) and (D), here the spatial distribution of electron density in the MO of the unpaired electron is significantly different. The positive sign of the $d_{x^2-y^2}$ orbital would then correspond to a decrease of electron density along the x axis and its corresponding increase along the y axis, as should be also the case under the conditions of the limiting decrease of the L–V–L valence angle.

2. Dependence of the Isotropic Hyperfine Interaction Constant A_i(V) on the Nature of the Ligand

As already mentioned, the Cp_2V d^1-complexes of types (A) and (B) differ from the complexes of types (C) and (D) by the dependence of the hyperfine interaction (HFI) constant on the nature of the additional one-electron ligands. The change in the quantity A_i(M) in transition metal complexes, where the unpaired electron is in a d orbital, has been attributed in EPR theory to the possible operation of two mechanisms: (1) the spin polarisation of the inner s orbitals and (2) the mixing of the MO_e with a MO of the complex having a suitable symmetry, in which there is a large contribution by the s orbital of the metal. In those cases where spin polarisation predominates, a correlation is observed between the change in the effective charge on the central atom (or the charge in the covalence of the metal–ligand bonds) and the quantity A_i;[99] under these conditions, an increase of the covalence of the bond entails an increase in the positive contribution to the A_i for transition elements of the first series. Bearing in mind the negative sign of A_i, for ^{51}V this should entail a decrease of $|A_i(V)|$. This type of linear relation had been noted earlier for titanium, vanadium, etc. complexes.[1] In the Cp_2V d^1-complexes of type (A), this mechanism is likewise the main one, since a linear correlation has been observed for such complexes between $|A_i(V)|$ and the sum $\sum_L (\chi_V - \chi_L)$ (Fig.4), which characterises the amount of ionic character (the covalence) of the V–L bonds. One should note that the correlation under discussion is observed when a rough approximation is used: the values of χ for the ligand atoms directly linked to vanadium are employed as the χ_L.

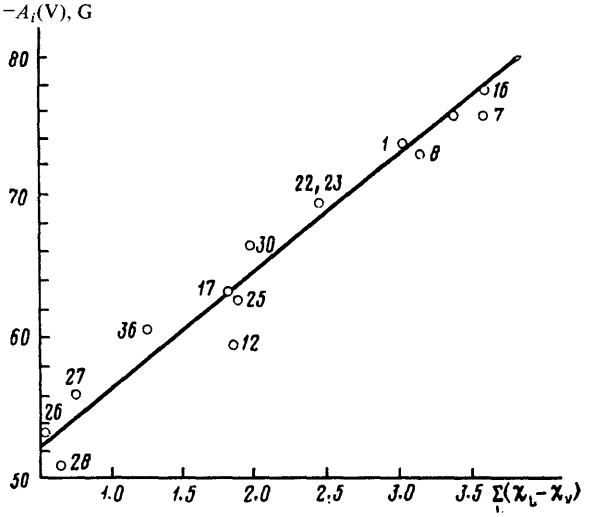


Figure 4. Dependence of the constant A_i(V) for Cp_2V d^1-complexes on the electronegativity of the ligands χ_L (χ is the Pauling electronegativity)[20] (for the significance of the numbering of the circles, see Table 1).

The linear relation between $\sum_L (\chi_V - \chi_L)$ and $|A_i|$ in a series of isostructural (within the limits of the immediate coordination environment of the vanadium atom) d^1-complexes of type (A) permits the conclusion that the HFI A_i(V) constants are additive. This makes it possible, in turn, to identify the ligands bound to vanadium in the complex from its EPR spectrum. As an illustration, Table 3 presents the experimental and calculated A_i(V) for certain mixed complexes

of the type $Cp_2VL_1L_2$; these values agree well with one another. As an example of the application of the rule of the additivity of the $A_i(V)$ for the identification of the Cp_2V d^1-complexes, one may consider the complex $Cp_2V(CN)(NCS)$ described by Morán and Fernandez.[13] The authors assumed that the complex has a structure corresponding to the presence of the isothiocyanato-ligand with a V–N bond. However, the value $|A_i(V)| = 59.43$ for this complex corresponds much better to the thiocyanato-complex $Cp_2V(CN)(SCN)$ with a V–S bond.

Table 3. Experimental isotropic parameters of the EPR spectra of certain Cp_2V d^1-complexes and the spectra calculated assuming additivity.[20]

Complex	g_i^e	$\|A_i(^{51}V)\|^e$	g_i^c	$\|A_i(^{51}V)\|^c$
$Cp_2V(Cl)Me$	1.9900	69.2	1.9898	68.7
$Cp_2V(Cl)CH_2SiMe_3$	1.9900	70.0	1.9896	69.4
$Cp_2V(Cl)SnEt_3$	1.9946	62.0	1.9954	62.2
$Cp_2V(Cl)GeEt_3$	1.9956	66.8	1.9950	64.9
$Cp_2V(CN)(NCS)$	1.9810	59.4	1.9900	66.7
$Cp_2V(CN)(SCN)$	—	—	1.9970	61.4
$Cp_2V(CH_2SiMe_3)SnEt_3$	1.9964	60 8	1.9979	57.5

*The experimental and calculated parameters are designated by the superscripts e and c respectively.

The additivity rule holds also for g_i for type (A) d^1-complexes, but with a lower degree of precision. The explanation is that, apart from the influence of the effective charge on vanadium, which alters the spin–orbit coupling constant, the quantity g_i is acted upon by at least two [sic] further factors: the contribution to g_i by the spin–orbit coupling. Both these factors also change on passing from one ligand to another and, although the overall trend in the variation of g_i is maintained (Fig.2), the overall operation of the three factors enumerated above complicates the character of the dependence of g_i on $\sum_L(\chi_V - \chi_L)$.

On passing from complexes of type (A) to those of types (C) and (D), the quantity $A_i(^{51}V)$ increases in succession and there is also a successive rise in g_i.[20] These changes are particularly clear in the carbon-containing d^1-complexes $Cp_2V(Alk)_2$, $Cp_2V(en)$, $Cp_2V(CO)$. Bearing in mind the negative sign of $A_i(V)$, its increase can be accounted for either by a decrease of spin density in the inner *s* orbitals of the vanadium or by an increase in the positive sign of the contribution of the 4*s* orbital to $A_i(V)$.

The amount of ionic character (covalence) of the V–L bonds can change on replacement of two one-electron ligands by one two-electron ligand with the same coordinating atom (carbon), but it is not possible to estimate it by a simple procedure, as has been done for complexes of type (A). One should only note that the approximation based on the use of the electronegativities of the coordinating atoms lacks significance in the given instance.

The most probable cause of the decrease of $|A_i(^{51}V)|$ on passing from complexes of type (A) to those of type (C) and further to complexes of type (D) may be the increase of the contribution of the 4s orbital to MO_e as a consequence of the mixing of the latter with a MO orbital of the same symmetry in which there is a large contribution by the 4*s* orbital. In the Cp_2V d^1-complexes there exist orbitals with a_1 symmetry, which are involved in the binding of the ligands L to Cp_2V and whose energies are close to that of MO_e. The effectiveness of their mixing with MO_e depends on the energy difference between the orbitals $\phi^e_{a_1}$ and ϕ_{a_1}, which should change following the replacement of ligands. If one takes into account the fact that, according to the results of quantum-chemical calculations[7] for the complex Cp_2VCl_2, the contribution of the 4*s* orbital of vanadium to MO_e is less than 1%, then the observed change in A_i for complexes of type (C) must be due to the increase of this contribution up to 2%, while that for the complexes of type (D) is caused by an increase up to 4%. (The value of A_i in the case of one unpaired electron in the 4*s* orbital of ^{51}V, quoted by Goodman and Raynor,[1] was used to calculate the amount of the admixture of the 4*s* orbital).

3. Hyperfine Interaction with Magnetic Nuclei of the Ligands in the Cp_2V d^1-Complexes

The idea of the transfer of spin density to the ligands in paramagnetic transition metal complexes has long been adopted in coordination chemistry. The fact that hyperfine interaction with the magnetic nuclei of the ligands has been observed by EPR has considerably promoted the development of this concept. Quantum-chemical calculations for the Cp_2V d^1-complexes yield high contributions of the ligands to MO_e. For the p_π orbitals of Cl or SH in Cp_2VCl_2 and $Cp_2V(SH)_2$, the contribution is approximately 22%.[7] However, hyperfine interaction with the magnetic ^{35}Cl and ^{37}Cl nuclei in the EPR spectrum of Cp_2VCl_2 as well as with the ^{79}Br and ^{81}Br nuclei in the Cp_2VBr_2 spectrum has not been observed,[9–12] but in a whole series of other complexes, where L = H, Me, Et, CH_2SiME_3, $SnET_3$, or $HgGe(C_6F_5)_3$ (Table 1), the change in spin density on the ligands has been confirmed experimentally by the presence of a signal due to the hyperfine interaction with the ^1H, ^{117}Sn, ^{119}Sn, ^{199}Hg, and ^{201}Hg nuclei in the EPR spectra. The hyperfine interaction with the ^{31}P and ^{75}As nuclei has been observed[29,30] in type (B) complexes, where the ligands were dialkyl phosphorodithioates and dialkyl arsenodithioates. For complexes of types (C) and (D), hyperfine interaction with the magnetic nuclei of the ligands was not observed. One should note that the additional hyperfine interaction with the magnetic nuclei of the ligands makes it possible to identify Cp_2V d^1-complexes with a high degree of reliability on the basis of their isotropic EPR spectra as a consequence of the highly characteristic nature of the latter. As an example, Fig.5 presents the isotropic EPR spectra of certain Cp_2V d^1-complexes.

The spin densities in the *s* orbitals of the ligands calculated from the experimental HFI constants are 2.9% (H), 2.7% (Me), and 1.9–2.5% ($SnEt_3$). Thus the overall spin density should not exceed 6% in the presence of two such ligands at the vanadium atom. According to the results of quantum-chemical calculations by a number of workers[6,7] for the Cp_2Ti, Cp_2V, Cp_2Cr, and Cp_2MO d^1-complexes, the contribution of the ligand *s* and *p* orbitals to MO_e is very insignificant. When these data are used as the starting point, one may conclude that the principal mechanism of the transfer of spin density to the α-atoms of the σ-bonded ligands is the

spin polarisation of the V–L–σ bonds under the influence of the unpaired electron in the *d* orbitals (the d_{z^2} orbital) of vanadium.

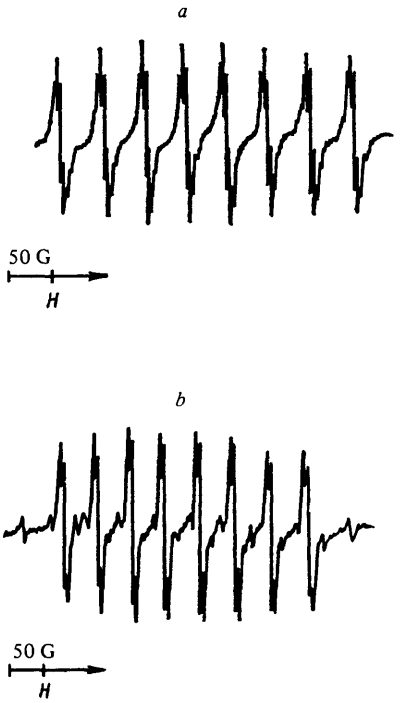


Figure 5. Isotropic EPR spectra of Cp_2V d^1-complexes: *a*) Cp_2VMe_2; *b*) $Cp_2V(CH_2SiMe_3)(SnEt_3)$ (toluene, 25 °C).[23]

In those cases where the α-atom of the ligands have p_π orbitals with a symmetry suitable for interaction with MO_e, a spin density should appear at the nucleus of the ligand atom as a result of the direct interaction between the ligand orbitals and the d_{z^2} orbital of the metal. Since in this case the binding to the metal is also achieved via the p_σ orbitals, the isotropic constant for the hyperfine interaction with the magnetic nuclei of the ligands is determined by the overall spin density of two different *p* orbitals of the ligand: p_π and p_σ. The two contributions have the opposite signs, because the direct delocalisation of the unpaired electron over the ligand leads to the appearance of a positive spin density in the p_π orbital, while spin polarisation induces a negative spin density in the p_σ orbital. An appreciable hyperfine interaction with the ^{35}Cl, ^{37}Cl, ^{79}Br, and ^{81}Br nuclei is absent in the complexes Cp_2VCl_2 and Cp_2VBr_2,[9–12] which indicates a low overall spin density in the *p* orbitals of these ligands, i.e. approximately equal contributions by each mechanism. If it is assumed (and this assumption is fairly valid) that the spin polarisation of the σ-bonds induces approximately equal spin densities in the orbitals (*s* and *p*) involved in the binding regardless of their nature, then it follows from the equality $\rho_{p_\pi} = \rho_{p_\sigma}$ that the overall contribution of the p_π orbitals of the ligands to the MO_e for the Cp_2V d^1-complexes should not exceed 6%. This differs significantly from the calculated data for Cp_2VCl_2 (22%) and Cp_2VS_5 (21%) obtained by Petersen et al.,[7] but agrees with the calculated data for the series of Cp_2V d^1-complexes quoted by Stewart and Porte.[6]

It is noteworthy that hyperfine interaction with the magnetic Cl and Br nuclei has been observed experimentally in the EPR spectra of the isoelectronic cationic complexes Cp_2Mo^+ and Cp_2W^+ and is appreciable: $A(Cl) = 3.1$ G and $A(Br) = 15.0$ and 21.9 G.[40] The spin polarisation contribution should not change significantly on passing from Cp_2V to the Cp_2Mo^+ and Cp_2W^+ complexes and the increase of $A(Cl)$ and $A(Br)$ should therefore be attributed to an increase in the direct contribution of the p_π orbitals of the halogens to MO_e. This conclusion agrees with the results of a calculation[7] indicating an increase in the contribution of the p_π ligand orbitals to MO_e for Cp_2MoCl_2 relative to Cp_2VCl_2.

Spin density can be transferred to the β-atoms of the ligands (the protons of the methyl and methylene groups in alkyl ligands) from the central atom via a mechanism similar to that of hyperconjugation in organic π-radicals.[41] This is indicated by the values of $A(H_\beta)$ which are comparable to $A(H_\alpha)$ for the hydride complex; in the case of the spin polarisation mechanism, the $A(H_\beta)$ must be much smaller, because the spin polarisation rapidly decays with increase of the number of "spin polarised" σ-bonds.

IV. EPR STUDY OF Cp_2V d^1-COMPLEXES IN SOLUTION

The data presented show that there is a close relation between EPR spectroscopic parameters and the structure of the Cp_2V d^1-complexes, which in some cases has a simple significance. This permits the EPR identification of the relatively unstable Cp_2V d^1-complexes formed as intermediates in various reactions and also determination of their structures.

1. Oxidative Addition to Cp_2V ($d^3 \rightarrow d^1$ Reactions)

Oxidative addition is the most typical reaction for Cp_2V. A wide variety of reagents, namely variable-valence metal salts, alkyl halides, chalcogenides, organic disulphides, alkynes, alkenes, and many other compounds interact with Cp_2V to form d^1-complexes (sometimes d^2-complexes). We may note that a large number of Cp_2V d^1-complexes with heterocumulenes have been synthesised and investigated during the last ten years by Floriani and co-workers (see, for example, Pasquali et al.[42]).

One of the first reactions involving oxidative addition to Cp_2V investigated was that with alkyl halides. A study[43] of the interaction of Cp_2V with MeI, EtBr, and $PhCH_2Cl$ led to the conclusion that the reaction proceeds in accordance with the equation

$$2Cp_2V + X-R \rightarrow Cp_2V-R + Cp_2V-X,$$

possibly via the intermediate formation of the extremely unstable complex $Cp_2V\begin{smallmatrix}R\\X\end{smallmatrix}$. Treatment of Cp_2V–R with an excess of R–X for a long time led to the appearance of Cp_2VX and R–R. The authors did not use the EPR method in their investigations, which apparently retarded for more than ten years the synthesis of dialkyl and alkyl halide Cp_2V d^1-complexes. The results of the above study[43] also apparently promoted the firm establishment of the idea that the high lability of such Cp_2V derivatives is due to the steric strain at the central atom.[44]

In reality, as shown[45] by monitoring the reaction of Cp_2V with RX with the aid of EPR, the latter proceeds in a more complex manner (Scheme 1):

Scheme 1

$$Cp_2V\langle^{R}_{R} + Cp_2VX;$$

$$(c)\uparrow Cp_2VR$$

$$Cp_2V + X{-}R \xrightarrow{(a)} Cp_2V\langle^{R}_{X} \xrightarrow[(b)]{Cp_2V} Cp_2V{-}R + Cp_2V{-}X;$$

$$(d)\downarrow$$

$$Cp_2V{-}X + [\dot{R}].$$

The first stage of the reaction is the synchronous oxidative addition of a molecule of RX to Cp_2V with formation of the alkyl halide d^1-complex $Cp_2V\langle^{R}_{X}$, which is stable. The difficulty of detecting it in solution by traditional methods is due to the reaction conditions and not to its increased lability. The presence in solution of Cp_2V, with which $Cp_2V\langle^{R}_{X}$ reacts very rapidly yielding Cp_2VR and Cp_2VX, is the main cause of the extremely low stationary concentration of $Cp_2V\langle^{R}_{X}$.[45] Under specially selected conditions, all the stages of the reaction can be realised separately. Thus slow dropwise addition at reduced temperatures (between -30° and -50 °C) of a solution of Cp_2V to a solution of RX taken in a large excess (more than 100-fold) makes it possible to reduce significantly the rate of the second stage (*b*) and promotes a steady detection of $Cp_2V\langle^{R}_{X}$ in solution by EPR.

We may note that, when alkyl iodides (MeI and Me_3SiCH_2I) are employed under the usual conditions, the interaction of Cp_2V with RX in stoichiometric proportions leads to the formation of appreciable amounts of the dialkyl complex Cp_2VR, which can be unambiguously identified from the EPR spectrum. It has been established, also by EPR, that it is formed as a result of the interaction of $Cp_2V\langle^{R}_{X}$ with Cp_2VR [stage (*c*)], accumulating in solution in the course of the reaction. The observation of this reaction made it possible to develop a new method of synthesis of dialkyl Cp_2V d^1-complexes, previously difficult to obtain, using Cp_2V and an alkyl halide as the starting materials.[45]

Another example of oxidative addition to Cp_2V, the understanding of the detailed mechanism of which would be impossible without the application of the EPR method, is provided by the interaction of Cp_2V with organic and organoelemental derivatives of cadmium and mercury. As early as 1975, it was shown[46] that the reaction of Cp_2V with $Cd(GeR_3)_2$ leads to the formation of Cp_2VGeR_3. The reaction mechanisms were assumed to involve the insertion of Cp_2V in the Cd–Ge bond (which is equivalent to oxidative addition to Cp_2V) with subsequent elimination of metallic cadmium and GeR_3. In a study[16] of the interaction of Cp_2V with $CdMe_2$, $CdEt_2$, $Cd(CH_2Ph)_2$, and $CdPh_2$ by EPR, the formation of Cp_2V d^1-complexes of the type Cp_2VR_2 was recorded. One of the complexes, namely dimethylvanadocene Cp_2VMe_2, was isolated in a crystalline form and thus proved to be the first reliably demonstrated dialkyl Cp_2V d^1-complex. Together with the data of Razuvaev et al.,[46] the results of this study led to the establishment of a scheme for the interaction of Cp_2V with organic and organoelemental derivatives of cadmium (Scheme 2):

Scheme 2

$$Cp_2V + X{-}Cd{-}X \rightarrow \left[Cp_2V\langle^{CdX}_{X}\right] \begin{cases} \rightarrow Cp_2V{-}X + Cd + [\dot{X}]; \\ \rightarrow Cp_2V\langle^{X}_{X} + Cd. \end{cases}$$

The primary product, a d^1-complex with a V–Cd bond, is merely a tentative intermediate in the above scheme. The final proof of the mechanism illustrated in Scheme 2 has been obtained recently[24] in a study of the reaction of Cp_2V with $Hg[Ge(C_6F_5)_3]_2$. As in the case of the reaction with Cp_2VGeR_3, the final product in this instance is the d^2-complex $Cp_2VGe(C_6F_5)_3$. A d^1-complex, which is a product of the oxidative addition of the organobimetallic derivative to Cp_2V, was detected by EPR in the course of the reaction. The presence of the mercury-containing substituent in this complex follows unambiguously from the analysis of the hyperfine structure of the EPR spectrum, which contains "satellite" components due to the interaction of the unpaired electron with magnetic Hg isotopes (Fig. 6).

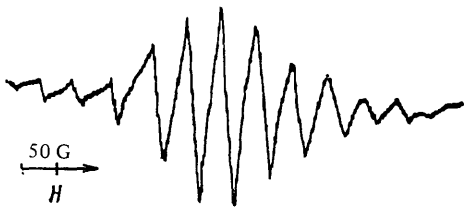


Figure 6. Isotropic EPR spectrum of $Cp_2V[Ge(C_6F_5)_3]$. $.HgGe(C_6F_5)_3$ (toluene, 10 °C).[24]

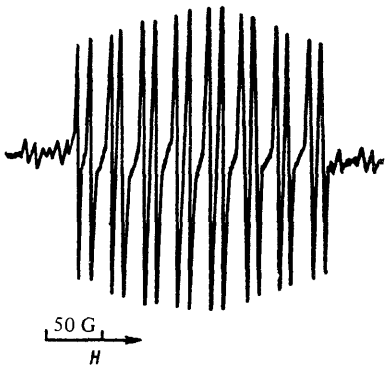


Figure 7. Isotropic EPR spectrum of $Cp_2V(H)SnEt_3$ (toluene, 25 °C).[23]

The first hydride d^1-complex $Cp_2V{-}Cp_2V(H)SnEt_3$, obtained as an intermediate in the reaction of Cp_2V with $HSnEt_3$, was detected by EPR.[23] The parameters of the observed EPR spectrum (Fig. 7) [g_i = 2.0007; $A_i(V)$ = -41.6 G; A_H = 14.6 G; A_{Sn} = 143 G] define unambiguously

the composition of the complex. Judging from the parameters of the anisotropic EPR spectrum, its structure is unusual for d^1-complexes with two η^1-ligands. The principal components of the $\bar{g}$ and $\bar{T}$ tensors of this complex differ appreciably from values typical for type (A) d^1-complexes and are close to the corresponding parameters of the type (C) d^1-complexes.

As mentioned above (in Section III), there is a relation between the spectroscopic parameters of the Cp_2V d^1-complexes and the structure, in particular the L–V–L valence angle. The d^1-complexes of type (C) usually differ from the d^1-complexes of type (A) by significantly smaller L–V–L valence angles. Judging from the EPR parameters, the compound $Cp_2V(H)SnEt_2$ should also differ in its structure from the usual d^1-complexes with two one-electron ligands, having a reduced L–V–L valence angle. This may be caused by the formation of an intramolecular bridging hydride bond H...Sn. The conclusions concerning the structure of the complex $Cp_2V(H)SnEt_3$, derived from the analysis of the spectroscopic data, cannot be tested by X-ray diffraction, since the complex investigated cannot be isolated from the reaction medium. However, a similar intramolecular hydride bond, leading to a decrease of the H–Nb–Sn valence angle to 58°, has been recently observed in a study of the complex $(Cp_2NbH)_2SnClEt$ by X-ray diffraction.[47]

In the presence of $HSnEt_3$ the hydride Cp_2V d^1-complex is converted, as shown by EPR, into a new d^1-complex containing two $SnEt_3$ groups, namely $Cp_2V(SnEt_3)$. This is indicated by the hyperfine structure of the EPR spectrum, corresponding to the interaction of the unpaired electron with the two equivalent tin nuclei.[23] The complex $Cp_2V.(SnEt_3)_2$ is also unstable and is converted after a time into Cp_2VSnEt_3 and hexaethyldistannane.[23]

The reaction of Cp_2V with $HSnEt_3$, investigated by EPR, is also of interest, because its mechanism may be similar in many details to the mechanism of the reaction of Cp_2V with alkanes (activation of C–H bonds[48]). Intermediates, with a structure analogous to that of the hydride complex $Cp_2V(H).SnEt_3$, have been postulated[48] in the reaction

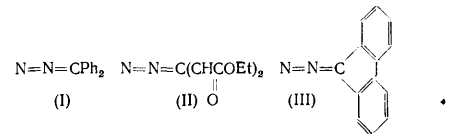
$$Cp_2V + CH_4 \rightarrow Cp_2V\begin{matrix}H\\Me\end{matrix}.$$

The existence of the fairly stable complex $Cp_2V(H)SnEt_3$ makes this hypothesis quite probable. We may note that the reaction of Cp_2V with $HSiCl_3$ described by Cardoso et al.,[49] which leads to the formation of a d^1-complex, can also proceed via the intermediate formation of a hydride silyl d^1-complex.

As already mentioned, the carbene-like properties of Cp^2V are very strikingly manifested in reactions with various substrates containing double and triple bonds. Many d^1-complexes of this type have been isolated in a pure state and their structures have been determined by X-ray diffraction. In all cases where the structure and EPR parameters of the complexes are known, complete agreement between them has been found. On the other hand, in certain EPR investigations of Cp_2V d^1-complexes the conclusions reached concerning the structure of the complexes are not entirely correct. Some of these controversial conclusions are discussed below.

It has been demonstrated convincingly[50] that the conclusions reached in an earlier investigation[51] of the structure of Cp_2V were based on an erroneous experiment. The isotropic EPR spectrum with $g_i = 2.00$ and $A_i(^{51}V) = 27.4$ G observed by the authors,[51] could not have been due to Cp_2V and must have been caused by the presence of an impurity. However, Prins[50] was also unable to assign the given spectrum to any one complex. On the basis of the conclusions reached in the present review, one may decide that the impurity signal, erroneously attributed to Cp_2V, referred to the Cp_2V d^1-complex of type (C) containing a two-electron η^2-ligand. It is difficult to arrive at conclusions about the nature of this ligand, since the experimental conditions are not fully known; it is quite likely that it might have been a carbene or a carbene-like ligand.

In considering reactions involving the oxidative addition of neutral ligands to Cp_2V one must deal with the study[35] of the interaction of Cp_2V with substituted diazomethanes:

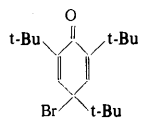


(I) (II) (III)

Depending on the diazomethane employed, EPR spectra of two types were observed: a spectrum with $g_i = 1.9918$ and $A_i(^{51}V) = 23$ G for (I) and one with $g_i = 1.9942$ (II) and 1.9953 (III) and $A_i(V) = 41$ G for (II) and (III). Despite the difference between the parameters, the authors[35] assigned the observed EPR spectra to g^1-complexes of one type, explaining the difference indicated in the spectra by the different degrees of delocalisation of the unpaired electron over the ligand. However, as shown above (Section II), the nature of the ligand in Cp_2V d^1-complexes of types (C) and (D) does not influence their EPR parameters to such a great extent (particularly as regards A_i). The observed difference between the constants $A_i(V)$ therefore requires a different explanation. The most natural cause of the difference between the EPR spectra is, in our view, the fact that they arise from complexes of different types. Judging from the value of $A_i(V)$, compound (I) is a type (D) d^1-complex with a two-electron η^1-ligand. Compounds (II) and (III) are type (C) d^1-complexes with a two-electron η^2-ligand.

2. Oxidation Reactions of Cp_2V d^2-Complexes ($d^2 \rightarrow d^1$ Reactions

The EPR method has been used particularly successfully in the study of reactions of the type $d^2 \rightarrow d^1$, namely reactions involving the oxidation of Cp_2V d^2-complexes. Compounds of the type Cp_2VX, where X = Cl, Br, alkyl, GeR_3, SnR_3, etc., are readily oxidised to Cp_2V d^1-complexes by various halogen-containing reagents, both inorganic and organic. The formal oxidation state of vanadium then increases from +3 to +4. The oxidation of Cp_2VCl, Cp_2VBr, Cp_2VMe, $Cp_2VCH_2SiMe_3$, Cp_2VGeEt_3, Cp_2VSnEt_3, and other Cp_2V d^2-complexes by reagents such as Ph_3CCl,

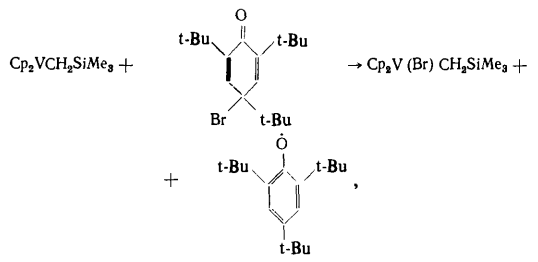


CuCl, $CuCl_2$, AgCl, AgBr, and Cp_2VCl_2 with formation of the corresponding Cp_2V d^1-complexes has been investigated[12,18,23] by EPR:

$$Cp_2VCl + Ph_3CCl \rightarrow Cp_2VCl_2 + Ph_3\dot{C}, \quad (4)$$

$$Cp_2VBr + CuCl \rightarrow Cp_2VBrCl + Cu, \quad (5)$$

$$Cp_2VMe + AgCl \rightarrow Cp_2V(Cl)Me + Ag, \quad (6)$$

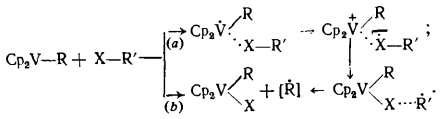


(7)

$$Cp_2VGeEt_3 + Cp_2VCl_2 \rightarrow Cp_2V(Cl)GeEt_3 + Cp_2VCl. \quad (8)$$

The occurrence of reactions (4) and (7), in which the oxidant is reduced to an organic free radical, clearly indicates a one-electron mechanism of the oxidation reaction. The oxidation-reduction reaction via a mechanism involving inner-sphere (bridge-type) one-electron transfer (with transfer of the bridging ligand) appears to be the most likely. This mechanism is formally equivalent to the transfer of a halogen atom [Scheme 3, pathway (*b*)].

Scheme 3



Reactions (4)–(8) indicate a high "affinity" of the Cp_2V d^2-complexes for one-electron reagents; free radicals may also be included among them. Hitherto there has been virtually no information in the literature about the reactions of Cp_2V d^2-complexes with free radicals. An exception is the study of Morán and Gayoso,[14] who showed that nitric oxide (NO), which is a stable radical, reacts with Cp_2VCl and Cp_2VBr, forming the d^1-complexes $Cp_2V(Cl)NO$ and $Cp_2V(Br)NO$ respectively. The study of the interaction of the Cp_2V d^2-complexes with free radicals is of undoubted interest, since reactions of this kind have been little investigated.

The oxidation-reduction reactions between Cp_2V d^2- and d^1-complexes, for example reaction (8), occupy a special place among the $d^2 \rightarrow d^1$ reactions. The complex Cp_2VCl_2 can also oxidise monoalkyl derivatives of the type Cp_2VR.[18] The mechanism of these reactions is evidently similar to that illustrated in Scheme 3. Mixed alkyl halide Cp_2V d^1-complexes can also participate in the oxidation-reduction $d^2 \rightarrow d^1$ reactions as oxidants. For example, $Cp_2V(Cl)Me$ can oxidise Cp_2VGeEt_3 and Cp_2VSnEt_3 to the corresponding d^1-complexes, being reduced at the same time to Cp_2VMe:[23]

$$Cp_2V\begin{matrix}Me\\Cl\end{matrix} + Cp_2V{-}R' \rightarrow Cp_2V{-}Me + Cp_2V\begin{matrix}R'\\Cl\end{matrix}. \quad (9)$$

The reaction between Cp_2V and alkyl halide d^1-complexes and alkyl d^2-complexes, which results in the formation of dialkyl d^1-complexes and monohalide d^2-complexes, proceeds differently:[18]

$$Cp_2V\begin{matrix}Cl\\R\end{matrix} + Cp_2V{-}R' \rightarrow Cp_2V\begin{matrix}R'\\R\end{matrix} + Cp_2VCl. \quad (10)$$

In terms of its formal features, reaction (10) is an exchange reaction in which the halogen in the d^1-complex is replaced by an alkyl group. However, its mechanism is evidently more complex and requires additional study.

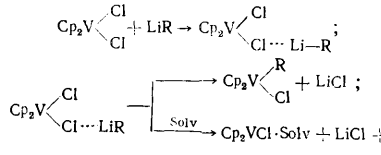
Investigation of reactions (4)–(10) by EPR showed that they are in many instances quantitative and can be used as preparative methods for the synthesis of mixed alkyl halide and dialkyl Cp_2V d^1-complex.[18] In the EPR variant, reactions of the type $d^2 \rightarrow d^1$ can be used as tests for the detection of Cp_2V d^2-complexes in solution. In particular, the formation of $Cp_2VGe(C_6F_5)_3$ and Cp_2VGePh_3 in the reactions of Cp_2V with $Hg[Ge(C_6F_5)_3]_2$ and $Hg(GePh_3)_2$ has been demonstrated in this way.[24]

3. Cp_2 d^1-Complexes in Exchange Reactions ($d^1 \rightarrow d^1$ Reactions)

The reactions of Cp_2VCl_2 with organometallic compounds, in particular with lithium, cadmium and aluminium compounds, have been most thoroughly investigated among processes of the type $d^1 \rightarrow d^1$ studied by EPR. Attempts to employ organolithium compounds for the synthesis of dialkyl complexes in solvating solvents have been frequently undertaken by various groups of investigators,[52] but they all gave a negative result—the reaction products were Cp_2V d^2-complexes, i.e. Cp_2VCl was reduced by LiR. These data served as a basis for the idea that the dialkyl Cp_2V d^1-complexes are unstable due to the steric hindrance around the central atom.[44]

The synthesis of Cp_2VMe_2, Cp_2VEt_2, and $Cp_2V(CH_2Ph)_2$ by the reaction of Cp_2V with organocadmium compounds showed that this concept is erroneous, after which Cp_2VMe_2 was also obtained by the exchange reaction from Cp_2VCl_2 and MeLi but in toluene instead of tetrahydrofuran.[53] There is no explanation in the literature of this type of strong dependence of the reaction pathway on the nature of the solvent. We believe that the main cause may be the influence of the solvating solvent on the intermediate complex formed in the first reaction stage (see Scheme 4).

Scheme 4



A second pathway, involving the oxidation-reduction reaction leading to the reduction of Cp_2VCl_2 to Cp_2VCl, competes in the presence of a solvating solvent, for example THF, with the "normal" pathway corresponding to the formal substitution of Cl^- by R^-. The solvation of the vanadium atom in the resulting d^2-complex by the solvent, which undoubtedly enters into the composition of the outer coordination sphere also of the initial compound Cp_2VCl_2, should play an important role in this process. Use of non-solvating solvents (for example toluene, as in the study of Foust and Rausch[53]) promotes the "normal" course of reaction.

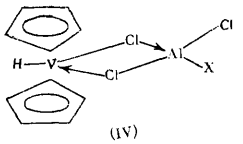
The OMC of cadmium and aluminium are also capable of interacting with Cp_2VCl_2, forming exchange products. The reaction of Cp_2VCl_2 with Et_2AlCl and other aluminium OMC has been studied in greatest detail. The EPR spectrum of the dialkyl vanadocene derivative has in fact been observed for the first time in one of these reactions. This concerns an EPR study[54] of a catalytic system based on Cp_2VCl_2 and an organoaluminium compound in which EPR spectra with a parameter $g_i = 1.992$ and $A_i \cong 62$ G, which evidently refer, as is now evident, to Cp_2VMe_2 and Cp_2VEt_2, were recorded. These products are obtained following the complete ligand exchange between Cp_2VCl_2 and the organoaluminium compound:

$$Cp_2VCl_2 + 2R_2AlCl \rightarrow Cp_2VR_2 + RAlCl_2 \quad (11)$$

Mixed alkyl halide Cp_2V d^1-complexes are also formed in such

reactions after the replacement of one halogen atom by an alkyl group.

A study of the reaction of Cp_2VCl_2 with Et_2AlCl led[54] to the observation of yet another unidentified EPR spectrum with the parameters $g_i = 1.997$ and $A_i = -39.5$ G. The same signal was later recorded in another study.[55] Having investigated in detail the isotropic and anisotropic EPR spectra, the authors[55] concluded that the EPR spectrum refers to a hydrido Cp_2V complex having the following structure:



(IV)

This hypothesis of such an unusual structure with parallel cyclopentadienyl rings is based on the "anomalous", from the authors' points of view,[55] parameters of the EPR spectrum of this complex compared with other Cp_2V d^1-complexes ($Cp_2.VCl_2$ and Cp_2VR_2). The disappearance of the isotropic EPR spectrum of the complex (IV) on treatment with THF or pyridine and the appearance of a new EPR spectrum with the parameters $g_i = 1.988$ and $A_i(^{51}V) = 70.3$ G was explained[55] by the conversion of compound (IV) into the hydrochloride d^1-complex $Cp_2V(H)Cl$ and was also regarded as evidence in support of the structure (IV), which the authors proposed. Treatment of a solution containing $Cp_2V(H)Cl$ with HCl led to the appearance of the spectrum of Cp_2VCl_2, while treatment with Et_2AlCl led to the spectrum of Cp_2VEt_2.

Comparison of the spectroscopic parameters quoted by Evans et al.[55] and the corresponding parameters of the EPR spectra of d^1-complexes of type (C) (with one two-electron η^2-ligand) and the known hydride Cp_2V and Cp_2Nb d^1-complexes, as well as the analysis of the chemical behaviour of the complexes showed that the interpretation of the two EPR spectra observed initially was erroneous.

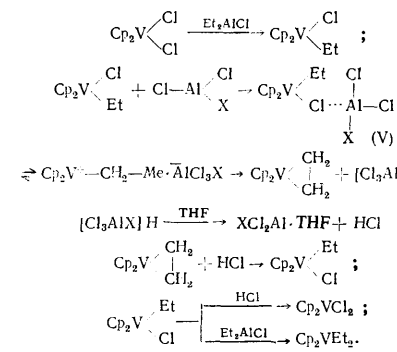
In the first place, in terms of their isotropic and anisotropic parameters [$g_i = 1.996$, $A_i(V) = -41.1$ G, $g_x = 2.001$, $g_y = 1.987$, $g_z = 2.000$, $T_x = -63.7$ G, $T_y = -70.5$ G, and $T_z = +1.09$ G], the primary EPR spectrum corresponds most closely to a Cp_2V d^1-complex with a two-electron η^2-ligand. Furthermore, one can assume that in the complex (IV) the hyperfine interaction with the hydrogen atom is weak and is therefore not manifested in the EPR spectrum (complexes of this type are unknown). As regards the complex $Cp_2V(H)Cl$, the absence from its spectrum of evidence for its hyperfine interaction with the ^1H nucleus is difficult to account for, since the $A(H)$ constants for the EPR spectra of other similar complexes [$Cp_2V(H)SnEt_3$ [23] and $Cp_2Nb(H)Cl$ [56]] are fairly large (>10 G) and the corresponding hyperfine structure should have been observed.

The absence of such hyperfine structure in the EPR spectra indicates an incorrect interpretation of the latter. The parameters of this spectrum correspond exactly to those of the spectrum of the known $Cp_2V(Cl)Et$ d^1-complex within the limits of the error of the measurement.

The new interpretation of the EPR spectra observed in the reaction of Cp_2VCl_2 with Et_2AlCl leads to a different mechanism for this reaction (Scheme 5), which differs from that proposed by Evans et al.[55]

The interaction of the reactants in the first stage of the reaction (the presence of small amounts of Et_2AlCl) leads to the replacement of one chlorine atom at the vanadium atom by the ethyl group with formation of the complex $Cp_2V(Cl)Et$, which can exist in solution both in a free state and in the form of a complex with an $XAlCl_2$ molecule. (The ability of Cp_2VCl_2 to form complexes with $AlCl_3$ is known[54]). An analogous complex, consisting of the reaction products, is formed on interaction of Cp_2VCl_2 with $Cd(GeR_3)_2$.[57] It is noteworthy that in solution $Cp_2V(Cl)GeR_3$ and its complex $Cp_2V(Cl)GeR_3.Cd(Cl)GeR_3$ are spectroscopically indistinguishable. Under the reaction conditions (with a hexane–CH_2Cl_2 mixture as the solvent), the complex (V) undergoes partial dissociation; proton transfer from $Cp_2V^+-CH_2-Me$ to $AlCl_3X^-$, which is evidently a stronger Lewis base than the ethylene complex formed, completes the process. In our view the "anomalous" EPR spectrum is in fact due to the ethylene Cp_2V d^1-complex.

Scheme 5



Under the influence of THF and the solution, the hydrogen chloride bound in the complex is liberated and reacts with the ethylene complex, converting it into $Cp_2V(Cl)Et$. Subsequent treatment with HCl converts $Cp_2V(Cl)Et$ into Cp_2VCl_2, while on interaction with Et_2AlCl alkylation proceeds further with formation of Cp_2VEt_2. The proposed mechanism undoubtedly requires special experimental confirmation, but it is much more consistent with the EPR data.[54,55] The results of a study[58] in which analogous reactions were observed between Cp_2MoCl_2 and Et_2AlCl may serve as its indirect confirmation.

Yet another interesting variety of $d^1 \rightarrow d^1$ reactions has been discovered[23] by EPR in a study of the interaction of Cp_2VEt_2 and $Cp_2V(CH_2SiMe_3)_2$ with $HSnEt_3$. This interaction leads to the formation of mixed d^1-complexes of the type $Cp_2V(R)SnEt_3$ under mild conditions. The second alkyl group is also not substituted under more severe conditions (−20 °C)—up to the decomposition temperatures of the initial dialkyl complexes. The mechanism of this reaction is still obscure and requires further study.

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In conclusion one should note that the EPR method will undoubtedly prove useful in the study of the structures of new Cp_2V d^1-complexes, whose chemistry is at present developing vigorously. Thus, much interesting information can be obtained from the study of the reactions, mentioned in this review, of Cp_2V with heterocumulenes which are coordinated to vanadium and in many cases undergo a series of consecutive reactions of the type $d^1 \rightarrow d^1$. Another interesting aspect of the chemistry of Cp_2V, involving reactions with unsaturated compounds containing Si=C, Si=Si, and Ge=Ge bonds, has so far been almost completely uninvestigated. It is to be expected that the high reactivity of Cp_2V with respect to multiple bonds will lead in this instance to the formation of complexes of type (C) with η^2-coordinated two-electron ligands, whose structure can be determined from the EPR parameters.

In the methodological sense, the conclusions reached in this review concerning the relation between the EPR parameters of the Cp_2V d^1-complexes and their structure can also be used in the study of the d^1-complexes of other transition metals (Ti, Zr, Hf, Nb, Ta, Mo, and W).

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The Stability of Organometallic Compounds During Their Synthesis and Decomposition

G.A.Domrachev, L.N.Zakharov, and Yu.A.Shevelev

Various aspects of the stability of organometallic compounds on the basis of the concept of the stability and structure of material systems are considered. The energy and steric factors in stability are discussed.
The bibliography includes 127 references.

CONTENTS

I. Introduction 739
II. Quantum-chemical stability 740
III. Thermodynamic stability 746
IV. Kinetic stability 747
V. The stability of organometallic compounds under non-equilibrium conditions 750

I. INTRODUCTION

The problem of the stability of organometallic compounds (OMC) arose during the dawn of the development of organometallic chemistry as a specific problem in the synthesis of OMC of non-transition[1] and transition[2] metals. A large number of thermally stable organoelemental compounds have been obtained with non-transition metals and non-metals. As regards transition metals, stable compounds have been obtained only in studies on the synthesis of polyaryl derivatives of chromium,[3] molybdenum,[4] and tungsten.[5] However, owing to the difficulty of the synthesis, further studies on these compounds were not performed up to 1954–1955. During these years polyphenylchromium compounds were again synthesised, their reductive decomposition was investigated, and their sandwich structure was confirmed.[6]

During the 1940s–1950s, the view arose that fully alkylated OMC of *d* and *f* elements are unstable and involatile on the basis of Nesmeyanov's,[7] Cotton's,[2] and Jaffé's[8] generalisations (the Mendeleev–Grosse–Nesmeyanov rule). Since the discovery[9] of biscyclopentadienyliron Cp_2Fe, having the sandwich structure, aromatic character, and a high stability (thermal, oxidative, etc.) the problem of the stability of OMC, particularly those of transition metals, has undergone a new development. Stable and volatile OMC of transition metals with many-centre bonds, the so-called polyhapto-(η^n)-derivatives of π-electron ligands and metals were synthesised.

At approximately the same time, Chatt's concept[10] of the stability of transition metal OMC containing a two-centre two-electron σ-bond with an alkyl or aryl ligand and having an electron shell of the next inert gas in Mendeleev's Table, built up by the electrons of electron-donating ligands (phosphines, etc.), was published. These views were confirmed by a series of experimental studies designed to synthesise σ-derivatives of platinum, palladium, and other metals.[11] Somewhat later, after the publication of the communications by Ziegler and Natta on the catalysis of the polymerisation of olefins,[12] experimental studies on the synthesis of alkyl (methyl, ethyl, etc.) derivatives of transition metals (titanium, chromium, manganese, etc.[11]) were published. Various investigators explained the low thermal stabilities of these compounds either in terms of thermodynamic or kinetic instability.

In their investigations of the problem of the kinetic stabilisation of σ-derivatives of transition metals, Wilkinson,[13] and Lappert and co-workers[14] achieved considerable successes in the synthesis of thermally stable OMC using bulky sterically hindered alkyl groups without C–H bonds in the β-position (in order to prevent the olefin-hydride decomposition of the OMC).

The problem of the stability of non-transition metal OMC has not arisen in quite such an acute form as for transition metals with the exception of the question of the stability of extravalence compounds, such as the pentacovalent derivatives of Group VA elements, and the question of the possibility of the olefin-hydride decomposition of OMC, for example, those of aluminium.

Studies on the radical decomposition *in vacuo* of lead, tin, and other metal alkyls,[15] on the photodecomposition in the gas phase of lead, mercury, and other metal alkyls,[16] and on the thermal reactions of alkyl and phenyl compounds of mercury, lead, tin in the condensed phase under hydrogen pressure in the presence and absence of catalysts, which have been described by Razuvaev,[17] may be regarded as some of the first investigations designed to determine the stability of non-transition metal OMC not as regards the possibility of their synthesis in principle but as regards the pathways and ease of decomposition of the OMC. Subsequently these studies were extended to the thermal and photochemical reactions of non-transition metal OMC in solution[18] and their aim became the demonstration of the formation of free radicals and their involvement in the reactions.[19]

In recent years the problem of the stability of OMC in relation to various decomposition processes arose anew in connection with the practical employment of OMC—for the preparation in the course of their decomposition of inorganic coatings and materials,[20,21] for the preparation of gaseous metals from OMC as active substances in gas lasers,[22,23] and also in connection with the extensive possibilities of the new methods of synthesis of OMC (the direct synthesis of OMC by the cocondensation of metal vapours with organic compounds,[24,25] the electrochemical synthesis of OMC,[26] the

radiation-chemical synthesis of OMC,[27] the plasma-chemical synthesis[28] and decomposition[29] of OMC in the gas phase). The application of these methods is frequently complicated by the instability of the OMC under the conditions of their synthesis or use, which gives rise to the necessity for the determination of the stability of OMC in various processes and under various conditions.

In the chemical literature there is no single combined approach to the problem of the stability of OMC. The authors only partially discussed the thermodynamic or kinetic aspect, the quantum-chemical aspect of the stability of OMC was considered in isolation from the former, and there have been virtually no studies on the stability of OMC under real non-equilibrium conditions in the presence of mass and energy fluxes. The aim of the present review is to consider critically, from a single standpoint, the concept of the stability of an isolated OMC molecule and also of systems incorporating OMC and their decomposition products in various states of aggregation, the energy and steric factors in the stability of OMC, and their manifestations under various conditions. Different aspects of the stability of OMC in the OMC synthetic and decomposition processes occurring under the following conditions are considered: thermal reactions involving uncharged (neutral) OMC species and the decomposition products; electron impact under the influence of an electric current with participation of charged (ionised) species; the effect of electromagnetic radiation with different energies and intensities (including laser radiation).

1. The Concept of the Stability of OMC

The concept of the stability of the state of a material system in time and space is fundamental. Its essential feature for a system of atoms or molecules having a definite order in space is the ability of the system to exist, subject to the influence of internal and external forces, in an equilibrium which corresponds to a definite energy level and their ability to return to a state of equilibrium after any kind of perturbation. The stability of the system in relation to various perturbations is almost always different and depends on the nature and character of the perturbations. When the latter is not specified, the stability of the system in relation to any perturbations is implied.

The set of stable bonds in a system of atoms and molecules ensuring the integrity and identity of the system itself in space and in time, constitutes the concept of the structure of the system. Hence the stability of the structure of a system is a characteristic of the stability of the system as a whole.

The stability of the structure of OMC is determined by two factors—energy and steric factors. The state of the system, for example an OMC molecule, is described by the solution of the Schroedinger equation, in which the eigenvalues of the energy (the energy factor) and the coordinate-temporal wave eigenfunctions (the steric factor) play equivalent roles. The eigenvalues of the energy and the steric localisation—delocalisation of the wave functions of the molecule can help to explain the energy and steric-specific features of the stability of OMC (for stationary time-independent solutions). Accordingly, in the analysis of the stability of OMC it is useful to consider in succession the energy and steric OMC stability factors in relation to various types of perturbations of the system or in relation to various types of OMC synthetic and decomposition reactions, in particular, the relation between the structure of OMC (the molecular structure, the structure of the condensed state) and stability and its influence on the reaction mechanism.

It is possible to differentiate four general aspects of the study of the stability of OMC, covering the molecular and electronic structures of OMC, all possible states of aggregation of OMC, their dynamics, and their interaction with fluxes (energy and mass fluxes): (1) the stability of an isolated OMC molecule (quantum-chemical stability); (2) the stability of systems incorporating OMC and their decomposition products in definite states of aggregation and at equilibrium (thermodynamic stability); (3) the dynamic stability of thermodynamically reversible systems incorporating OMC and their decomposition products in definite states of aggregation at equilibrium and in the vicinity of equilibrium and the rate of approach to equilibrium by the system (kinetic stability); (4) dynamic stability of thermodynamically irreversible systems consisting of OMC and their decomposition products in definite states of aggregation in the presence of mass and energy fluxes both near and far from thermodynamic equilibrium (the formation and stability of dissipative structures, macrokinetic aspect).

The first two aspects refer to the description of systems having a time-independent spatial structure, while the second two characterise the stability of systems with a time-dependent spatial-temporal structure.

II. QUANTUM-CHEMICAL STABILITY

We shall consider the quantum-chemical stability of OMC, concentrating attention initially on the energy factor (the stability of the electronic structure of the OMC molecule) and on the steric factor (the stability of the molecular structure of the OMC) and also on the description of the possible states of OMC with the aid of potential energy surfaces, the description including both factors. In conclusion we shall discuss the main types of possible perturbations of the OMC molecule which determine its stability.

The main criterion of the possible existence of an isolated OMC molecule (*in vacuo*) is the quantum-chemical stability. A quantum-chemical estimation of the stability of the OMC molecule presupposes the consideration of electron shell stability (the electronic configuration, structure) of the molecule relative to the stability of the electron shells of isolated molecules (species) of the decomposition products considered in valence states. Overall, the quantum-chemical stability of OMC is determined,[30] firstly, by the electronic configuration (structure), of the OMC molecule, i.e. the distribution of electrons among the bonding, non-bonding, and antibonding MO; secondly, the binding energy in each MO, i.e. the decrease of the energy of the bonding MO relative to the energy of the constituent orbitals of the isolated fragments; thirdly, the non-bonding interactions (usually repulsive), which characterise the steric hindrance in the OMC molecule and determine its steric structure.

There exist a series of theoretical and empirical criteria of electron shell stability in OMC and their molecules, characterising their quantum-chemical stability. For the majority of ions of the elements in the Periodic System, metal carbonyls, and the OMC of non-transition and transition metals, there exists a rule which states that a closed electron shell is stable. For compounds having a central atom of an element, the most stable (closed) electron shell is that which attains the electronic structure of the shell of the next inert gas in Mendeleev's Table by employing electrons of all the ligands involved in the bonds with the element (the extension of Sidgwick's rule[31] to ions). The most stable compounds are formed precisely in conformity with the "inert gas rule" (for example, ferrocene, dibenzenechromium, virtually all the

transition metal carbonyls, especially mixed cyclopentadienyl- or arene-metal carbonyls, etc.), although there exist many exceptions to this rule. The inert gas rule is the overall consequence of Hund's rule,[32] which states that unoccupied, half-occupied, and wholly occupied subshells are stable (the *s*, *p*, *d*, and *f* shells).

In organic complexes of metals and in OMC molecules this stability criterion leads to the stabilisation of both low-spin and high-spin states, for example, in $(C_5H_5)_2Mn$ stabilisation of the configuration with maximum spin (five unpaired electrons) is energetically favourable, whereas in ferrocene as well as in the ferrocenium cation, which is isoelectronic with manganocene, stabilisation of the low spin configuration is observed.

A special case of the overall effect of the stabilisation of the electronic structures of derivatives of non-transition elements is the octet rule (involving the s^2p^6 electronic configuration).[30]

Mendeleev's remark, contained in the early editions of "Principles of Chemistry" (up to the eighth),[33] namely that only the elements in the odd series are capable of forming organometallic compounds and that, when an element forms a hydrogen compound EH_x, it also forms organometallic compounds ER_x, constitutes one of the first formulations of the OMC stability rules. Grosse[34] assumed that only the elements whose valence electrons are located in levels with the same principal quantum number, i.e. non-transition elements, give rise to typical alkyl compounds.

On the basis of a survey of extensive experimental data, Nesmeyanov[7] formulated the following rule: "alkyl groups are bound fairly stably to an element only via *sp*-valence levels. The presence in the atoms of even unused *d* or *f* valence electrons cause a sharp weakening of the stability of the resulting alkyl derivatives, renders them atypical and involatile, and altogether prevents their existence". In his generalisations,[7,35] Nesmeyanov discussed the thermal instability and stability of OMC, which he estimated either on the basis of the possibility of the existence of compounds at room temperature or at the decomposition temperature.

The Mendeleev–Grosse–Nesmeyanov rule has received a theoretical quantum-chemical justification in Jaffé's studies.[8] According to Jaffé, the M–C σ-bonds are weaker for transition metals than for all the principal elements and their strength increases with increasing *s* character of the hybrid carbon orbitals of the group linked to the metal: sp^3 (alkyls) < sp^2 (aryls) < *sp* (acetylides). When aryl groups are bound to transition metals, there is a possibility of additional strengthening of the bond and there is also the formation of π-bonds, both donor–acceptor Ar → M bonds of the types $2p_\pi \rightarrow np_\pi$ and $2p_\pi \rightarrow (n-1)d_\pi$ (for transition metals) or $2p_\pi \rightarrow nd_\pi$ (for non-transition elements), and dative M → Ar bonds (via the pairs of electrons of the d_π orbitals of the metal). In the experimental studies of Chatt and co-workers[10] on the stability of organic derivatives of Group VIII metals it was established that the OMC is stable in relation to thermal dissociation when all the bonding MO are populated by pairs of electrons, for example, the electrons of phosphine, amine, or carbonyl ligands. In this case the carbon-transition metal σ-bond is stabilised and there is a possibility of isolating stable OMC, for example, $CH_3Mn(CO)_5$, $Alk_2Ni(PR_3)_2$, etc.

The OMC stability rules quoted above refer to the degree of population of the bonding, non-bonding, and anti-bonding MO. If all the bonding MO are populated by electron pairs and the non-bonding MO, if such exist, are not orbitals of the π-system but constitute the orbitals of unshared electron pairs of the ligand heteroatoms or the orbitals of the electrons in the metal atom which are non-bonding in relation to ligands, then such an electronic configuration (structure) of the OMC should be stable in the quantum-chemical aspect (analogously to Hückel's rule concerning the stability of aromatic systems). The stability of the electronic structure of OMC, expressed in terms of these theoretical and empirical rules, is based on the fact that, on formation of the entire system of chemical bonds in the molecule between the metal and the ligands, there is an overall energy decrease of all the electrons in the molecule relative to the isolated ligands and the metal atom. This decrease corresponds to the stabilisation of the electron shell both via the formation of chemical bonds and because the closed electron shell is favoured by energy factors.

The methods of ultraviolet, X-ray, and photoelectron (PES) spectroscopy[36] make it possible to determine experimentally the vertical and adiabatic ionisation potentials of the molecules and to find the sequence of energy levels of the electrons involved in the M–C, C–C, C–H, etc. bonds and also of the non-bonding electrons of the metals, which yields complete information about the energy distribution of the electrons in OMC. On the basis of experimental studies of mononuclear and polynuclear OMC of non-transition and transition metals,[37–39] the sequences of the energy levels of the electrons in OMC have been established. Under the conditions where Koopman's theorem is applicable, this yields an idea about the sequence of the energies of the one-electron molecular orbitals[40] and, when Koopman's theorem is inapplicable, it yields the sequence of the energies of the multielectron levels of the molecule.

The non-bonding electrons of the metal are usually located in the highest of the occupied MO and below these are the MO which correspond to the electrons involved in the metal–metal σ-bonds or the metal–ligand δ- and π-bonds. These are followed by the strong bonding MO corresponding to the metal–ligand (group) σ-bonds and the σ-bonds within the ligands (C–C and C–H).

Consideration of the OMC stepwise dissociation (decomposition) process shows that each reaction stage can be modelled by means of a two-particle approximation and, by analogy with diatomic molecules, one can assume that the dependence of the energy on the metal–ligand distance is described by a potential curve resembling the Morse curve. In this case one can speak of the dissociation energies of specific bonds (D_1, D_2, etc.) formed by the metal-containing fragment of the OMC molecule and the ligand:

$$R_nM \rightarrow R_{n-1}M \ldots R \xrightarrow{D_1} R_{n-1}M + R;$$
$$R_{n-1}M \rightarrow R_{n-2}M \ldots R \xrightarrow{D_2} R_{n-2}M + R \quad \text{etc.}$$

The quantities D_n are determined by mass-spectrometric or thermochemical methods. The average bond dissociation energies *D*, determined experimentally for the gas-phase total dissociation of the OMC, are used in many cases as a measure of the strength of the metal–ligand bond in the OMC:[41–43]

$$R_nM\,(\text{gas}) \overset{n\bar{D}}{\rightleftarrows} M\,(\text{gas}) + nR\,(\text{gas}). \qquad (1)$$

For the majority of the metals investigated, the values of D_n or *D* are always much greater than zero and usually amount to between 20 and 100 kcal mol^{-1} and more.[41–43] Consequently the formation of isolated OMC molecules is energetically favourable. On the other hand, the stability of the molecules produced depends on the stability of the electronic structure acquired by the metal in the OMC and on the stability of the steric molecular structure of the OMC.

Proceeding now to the consideration of the stability of the molecular structure of OMC, we may note that the latter depends on the spatial distribution of the electron density associated with the chemical bonds, the unshared electron

pairs, and the non-valence interactions between ligands which are not linked by bonds, i.e. on the steric factor. When the non-valence interactions do not give rise to steric hindrance to the formation of the molecular structure, the stability of the latter is determined by the extent to which the corresponding spatial distribution of electron density and the atomic nuclei is energetically favourable, this being determined by the structure of the electron shells of the OMC, the metal atom, and the ligands.

If the ligands form chemical bonds with the metal via one of their sp^3, sp^2, or sp orbitals, then the electronic structure of the OMC of non-transition and transition metals represents[44] a set of two-electron two-centre σ-bonds, one of which is localised on each ligand. The number of such bonds, their spatial distribution, and the stability of the OMC are determined by the structure of the electron shell of the metal, the number of valence electrons, and the number and type of unoccupied atomic orbitals (AO) of the metal. For ligands with sp^2 and sp valence orbitals, weak or strong π-bonds,[44] involved in p_π–p_π or p_π–d_π interactions, may be formed in addition to the σ-bonds. In order to find the most stable configurations of molecules of the type MR_n use is made of Pauling's[45] and Murrell's[46] maximum overlap method, which has been successfully developed by other workers.[47–49]

Organic ligands containing an unsaturated π-electron system (η^n-ligands: alkenes, alkynes, allyl, cyclobutadiene, cyclopentadiene and cyclopentadienyl, benzene, etc.) give rise to considerable possibilities for the formation of many-centre metal–ligand bonds in OMC molecules. Many-centre two-electron σ-, π-, and δ-bonds are usually formed along the principal symmetry axis of the ligand and in the case of transition metals such organic derivatives have a sandwich structure.[11]

The strength of the bonds between polyhapto-ligands and transition metal atoms is determined by the total number of two-electron many-centre bonds formed with the given ligand and reaches a maximum on formation of the maximum number of the possible bonds. With increase of the metal–ligand distance, the strength of the π- and especially δ-bonds diminishes sharply in contrast to the σ-bond, which acts over a longer range.[50]

The nature of the bonds between polyhapto-ligands and non-transition metals such as silicon, germanium, and tin is close to that of the analogous bonds with transition metals, i.e. also delocalised over the ligand,[51,52] although, by virtue of the lack of the ability of the electron shells of these metals to form many-centre π- and δ-bonds, they are comparatively weak σ-bonds.[51]

The stability of OMC containing bonds between polyhapto-ligands and transition metals is frequently strikingly high. Compounds in the molecules of which all the bonding MO are occupied by pairs of electrons (in many cases such filling of the MO corresponds to the inert gas rule) are especially stable.

The spatial distribution of the many-centre bonds in the OMC molecule depends, analogously to the two-centre σ-bonds, on the electronic structure of the metal and also on the presence or absence of steric hindrance owing to the repulsion of the non-bonded ligands (the effect of the latter is the steric and energetic non-equivalence of the ligands and of their bonds with the metal, for example, the existence of different numbers of η^5- and η^1-C_5H_5 ligands in compounds of the type $(C_5H_5)_4M$ (M = Ti, Zr, or Hf),[53] etc.

Overall, the delocalisation of electrons over many centres, which leads to the formation of a many-centre transition metal–ligand bond, increases significantly the stability of OMC. Stabilisation of labile metal–carbon bonds also results from the formation of a chelate ring via a neighbouring (usually in the β-position within the substituent group or in the *ortho*-position in a phenyl substituent) electron-donating group of the type of $\ddot{N}R_2$, $\ddot{O}R$, and $\ddot{P}R_2$.[54]

The next type of intramolecular interactions influencing the stability of OMC molecules are the so-called additional interactions, intermediate between valence (bonding) and non-valence (repulsive) interactions.[55] By binding the metal atom to the substituent group (ligand) or the ligands to one another, these interactions increase the quantum-chemical stability of the OMC, as happens, for example, in the case of $[(C_6F_5)_3Ge]_2Hg$.[56]

As already mentioned, the non-bonding interactions, namely the repulsions between the substituent groups (ligands) not linked by valence bonds, the unshared electron pairs, and atomic nuclei, play an important role in the formation of the molecular structure of the OMC and its stability. They can influence appreciably the extent of the bonding and additional interactions up to complete blocking of the possibility of bond formation. The non-bonding interactions in the OMC molecule lead, on the one hand, to the steric shielding of the metal atom (or a group of metal atoms in polynuclear OMC and metal clusters) by substituents (ligands) (this characteristic of the OMC molecule will be used subsequently when the stability of the state of aggregation of the OMC are considered) and, on the other hand, such interactions can lead to steric hindrance to the formation of metal–ligand bonds. The first effect always increases the stability of the state of aggregation of OMC (see below), while the second reduces the stability of the OMC molecule.

The influence of non-bonding interactions (steric effects) on the molecular structure of the OMC and its stability has been noted in many communications (see, for example, Wilkinson[13] and Davidson et al[14]), but few systematic studies of this problem have been made, (see, for example, Refs.57–60).

There exist several methods for the quantitative estimation of the bulk of the substituents (ligands) and hence of the extent of non-bonding interactions in OMC molecules.[58–60] One of these, described by the present authors,[58] consists in calculating the solid angles formed by the substituents (ligands) with the vertex at the metal atom (Fig.1*a*). Cylindrical projections of the molecule can be usefully employed for such purposes in the molecules of polynuclear OMC containing chains of metal atoms.[58] It is possible to use the method proposed also for transition metal clusters. Fig.1*b* presents the dependence of the solid angles q on the M–X distance, where X is an atom of the substituent (ligand) linked to the metal atom M (for certain ligands). The sum of the solid angles for all the substituents (ligands) in the molecule

$$Q = \sum_{i=1}^{n} q_i,$$

where n is the number of substituents (ligands) in the molecule, can be used for the *a priori* estimation of the possible existence of molecules from the standpoint of steric hindrance due to non-bonding interactions, because this sum should be less than or equal to half the solid angle 4π. The quantity $Q > 4\pi$ indicates the possibility of steric hindrance and hence a low probability of formation or stability of the suggested OMC molecule. Conversely, the quantity $Q < 4\pi$ indicates the absence of steric hindrance to the formation of the molecule and at the same time characterises the degree of shielding of the metal atom in the latter by the substituents (ligands).

The energy and steric factors together determine the electronic and steric molecular structures of the OMC and their separation in merely methodological in character. Indeed,

the set of solutions of the Schrödinger equation with variation of the steric parameters (coordinates of the atoms or fragments of the OMC molecule) defines the potential energy surface (PES), describing all the states of the OMC molecule in terms of spatial coordinates. Equilibrium interatomic (interfragment) distances, which correspond to equilibrium between the forces of attraction and repulsion between the fragments of the molecule, correspond to the minimum on the PES (i.e. to a stable state of the OMC). Allowance for the non-bonding interactions of the non-bonded fragments of the OMC molecule in the calculation of the PES makes it possible to estimate the most favourable steric molecular structure of the OMC[61] and hence obtain an idea about the stability of the molecule.

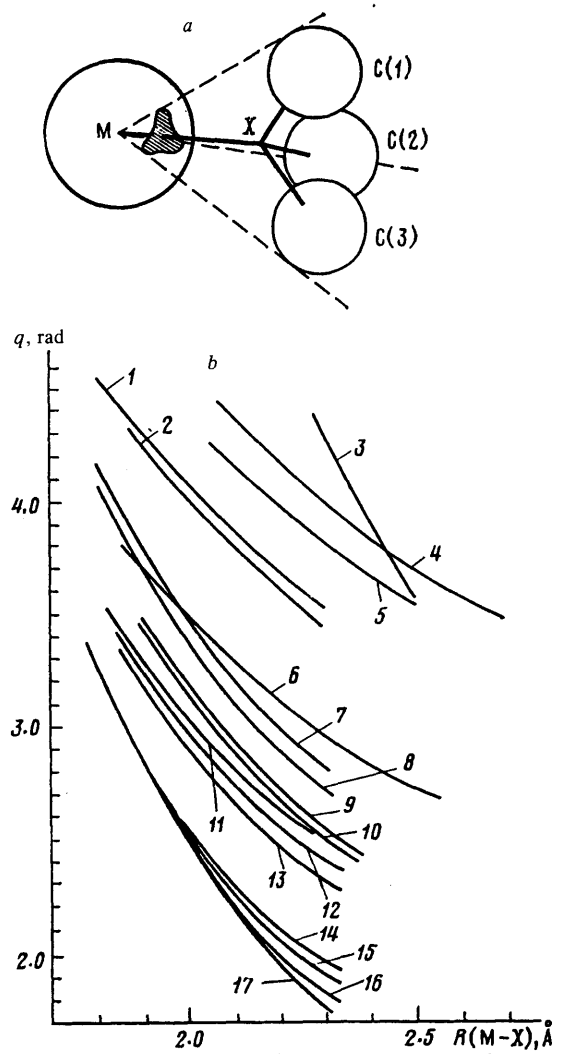

Figure 1. *a*) Scheme illustrating the structure of the solid angle *q* made by the substituent; *b*) dependence of the solid angle *q* on the distance R(M–X) for certain common substituents and ligands (an ideal tetrahedral or planar-trigonal coordination has been assumed for the atom X of the substituent).[58] Substituents: 1) CPh_3; 2) $CH(SiMe_3)_2$; 3) η^5-Cp; 4) $SiPh_3^F$; 5) $Si(t\text{-}Bu)_3$; 6) PPh_3; 7) CH_2CMe_3; 8) 2,4,6-$Me_3C_6H_2$; 9) CH_2SiMe_3; 10) CF_2CF_3; 11) CCl_3; 12) CMe_3; 13) ferrocenyl; 14) η^1-Ph; 15) CF_3; 16) η^1-Cp; 17) Me, Et.

The stability of the electronic structure of the molecule on the PES is determined by the extent to which the transition of the electronic structure of the OMC from the surface corresponding to the ground electronic state to one corresponding to excited electronic states, including dissociative states, is hindered. Molecules, for which the intersection of the PES for the ground state with the PES for the excited states requires a considerable energy expenditure and deformation of the molecule (which is extremely probable for steep walls of the potential well on the PES of the OMC) apparently have stable electronic and molecular structures. In those cases where a potential well with sloping walls corresponds to the ground state of the OMC and, at the same time the PES for the ground state has no close intersections with the PES for the excited electronic states, the electronic structure of the OMC is stable and the molecular structure is labile relative to changes in the distances between the fragments.

We shall now consider the susceptibility of the OMC molecule to perturbations in the structure, which displace it from its position of stable equilibrium. The response of the OMC molecule to perturbation depends both on the type of the latter and on the nature of the bonds in the molecule. The following principal types of perturbations in the OMC molecular structure, characterising its stability, can be differentiated: (1) movement of a fragment and ligand forming part of the OMC molecule, which leads to homopolar bond dissociation with formation of neutral species; (2) movement of a fragment and ligand forming part of the OMC molecule leading to heteropolar bond dissociation with formation of charged species (ions) with opposite charges; (3) shifts of electron density and nuclei in the OMC molecule in opposite directions leading to the ionisation of the molecule to give the cation OMC^+ and an electron (characterised by the OMC ionisation potential and the redox potential in solution).

From general considerations, it is easy to conclude that the polarity of the metal–ligand bonds in the OMC as well as the bond energies play an important role in determining the ease of each of the three perturbation processes. A number of conclusions concerning the polarity of the bonds and the character of the MO in the OMC of non-transition and transition metals can be arrived at by assuming, in conformity with the Koopman's theorem,[40] that the one-electron MO may be responsible for the ionisation potentials of the molecule.[21]

A characteristic feature of non-transition metals whose ionisation potentials (IP_M) are of the order 4–8 eV is the reaction with organic radicals, whose ionisation potentials (IP_R) are about 8–10 eV, to form OMC which have $IP_{OMC} > IP_M$ (for $IP_R > IP_M$) in the absence of non-bonding electrons in the metal and a populated d^{10} shell in post-transition metals (Fig.2*a*).[21] As a consequence of the electropositivity of the metal, the contribution of the substituent orbital to the populated bonding MO is higher than would correspond to the formation of a polar M–R bond with a negative charge on the substituent. For similar ionisation potentials $IP_M \cong IP_R$, the M–R bond is significantly non-polar (covalent), although $IP_{OMC} > IP_M \cong IP_R$. For metals and substituents for which $IP_M > IP_R$, the negative charge of the dipole of the M–R polar bond is localised at the metal atom and the bonding MO involves a predominant contribution by the atomic orbital of the metal.

For transition metals having $IP_M \cong 7$–8 eV combined with organic π–η^n-ligands, for which $IP_R = 8$–9 eV, the situation is somewhat altered. Since transition metals have *d* electrons and unfilled atomic orbitals, while the π–η^n-ligands have filled and unfilled MO, it follows that, together with covalent bonds, there is a possibility of the formation of both donor–acceptor and dative bonds (Fig.2*b*).[21] The formation of donor–acceptor bonds, using the electron pairs of the ligands

and the AO of the metal, requires, as an essential condition, the rearrangement of the electron shell of the metal with liberation of the lowest AO having the appropriate symmetry and the filling, as a rule, of the d_δ and d_σ orbitals of the metals, among which the d_δ orbitals are involved in the formation of dative bonds with the antibonding MO of the ligands.

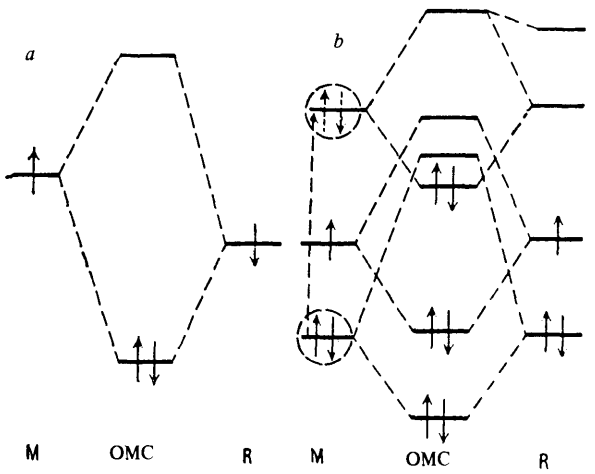

Figure 2. Molecular orbital diagrams for the OMC of non-transition (*a*) and transition (*b*) metals;[21] M = metal; R = substituent or ligand; the dashed arrow denotes the rearrangement of the electron shell.

In most cases the lowest bonding MO of the OMC molecule, corresponding to the donor–acceptor bonds, involve a large contribution by the ligand MO; MO with moderate energies, corresponding to covalent bonds, involve approximately equal contributions by the AO of the metal and the MO of the ligands, while the highest MO usually have the character of non-bonding or weakly bonding MO localised at the metal, since $IP_M \cong 7-8$ eV and the ionisation potential of the antibonding ligand MO is usually ~3–4 eV. Hence one can reach two conclusions. Firstly, since the formation of the optimum number of bonds ensuring the minimum energy of the OMC molecule requires a rearrangement of the ground electronic state of the transition metal to give an excited state, the upper electrons should be distributed in higher energy levels than the electrons of the free metal atom and should be non-bonding or weakly bonding in character. Secondly, the effective charge on the metal atom can be estimated from the energies of these non-bonding electrons. A survey of data for the IP_{OMC} of transitions metals[21,41] shows that $IP_{OMC} \leq IP_M$. This indicates an insignificant deviation of the charge on the metal from zero, which has in fact been confirmed by calculations yielding results close to the experimental data, for example, for ferrocene[62] and dibenzenechromium.[63–66] Thus, predominantly non-polar (covalent) bonds are observed in many η^n-derivatives of transition metals, with the exception of a number of compounds of the type of manganocene and cyclopentadienyl derivatives of the lanthanides, as a consequence of the mutual compensation of the shifts of electron density owing to donor-acceptor and dative interactions.

Having adopted the polarity of the metal–ligand (substituent) bond as the factor influencing the ease of both dissociation [homopolar (2) or heteropolar (3)] and ionisation processes, we shall now consider the characteristics of the energy relations of these processes.[66–73] If it is assumed that the OMC contains a polar $M^{\delta+}-R^{\delta-}$ bond, then its possible dissociation processes can be formulated as follows:

$$M^{\delta+}—R^{\delta-} \rightarrow M^0—R^0 \rightarrow M^0+R^0; \quad (2)$$

$$M^{\delta+}—R^{\delta-} \rightarrow F^+ + R^-. \quad (3)$$

Dissociation via scheme (2) should be accompanied by the abolition of the polar bond in the course of its dissociation.[20,21,66,73] Estimation of the energy of the displacement of the electron pair in the polar bond (the ionic component ΔE) by the method of Razuvaev et al[20] showed that different M–R bonds have different values of ΔE. Small, nearly zero values of ΔE are favourable for reaction (2), while higher values of ΔE hinder it.[20] Conversely, higher values of ΔE favour reaction (3) while low values hinder it. The ionisation process is promoted by low values of IP_{OMC} and also by high energies of the exciting quanta. The conditions associated with thermal reactions or multiquantum infrared excitation correspond to the first type of perturbation, which is milder and leads to homopolar dissociation. As a consequence of the greater strength of the more ionic bond, reaction (3) is promoted as a result of excitation by higher energy quanta (electron impact and ultraviolet, X-ray, and γ-ray quanta) or by the delocalisation of the separating charges on solvation and on exposure to an electric current in solution.[67–71]

III. THERMODYNAMIC STABILITY

The quantum-chemical stability of the OMC considered above determines the possibility, in principle, of the formation and existence of an isolated OMC molecule. If such a possibility exists, then the set of molecules forming a definite state of aggregation of the given substance can be stable in relation to any one decomposition process under some conditions, while under others it is unstable. The state of equilibrium in the thermodynamically reversible OMC $\rightleftarrows$ decomposition product system, the decomposition products involving different combinations of states of aggregation, is a measure of the thermodynamic stability of the OMC in relation to any decomposition process and is determined by the sign and magnitude of the change in the Gibbs free energy ΔG in this process.

The thermodynamic stability of coordination and organometallic compounds in relation to heteropolar dissociation into gaseous or solvated ions, i.e.

$$R_nM \rightleftarrows nR^- + M^{n+} \quad (4)$$

differs significantly from that for the homopolar dissociation into gaseous or solvated uncharges species (decomposition products):

$$R_nM \rightleftarrows nR + M. \quad (5)$$

Since reaction (4) in the gas phase involves charge separation, it is very greatly hindered by energy factors, i.e. it has high values of ΔH and is facilitated by solvation of the ions in solution. (There exists an extensive literature on the stability of coordination compounds in solution in relation

to reaction (4).[67-71] In view of the much lower values of ΔH, in the gas phase at temperatures up to ~1000° virtually the only dissociation process is the homopolar reaction (5).

Accordingly, the thermal stability, frequently discussed as a general characteristic of the OMC,[7,35,72] should be defined as the stability of OMC in relation to reaction (5) in all the aspects (quantum-chemical, etc.) discussed in this review. As a criterion of the thermal stability of OMC in its thermodynamic aspect, one must consider the presence of equilibrium in the homopolar bond dissociation process,[20,73] with formation of uncharged species: the metal and radicals (for ligands with an odd number of electrons involved in the formation of the bond) or molecules (for ligands with an even number of electrons participating in the formation of the bond). The reverse reaction in this case involves the synthesis of OMC from the decomposition products.

For a general consideration of the thermodynamic stability of OMC in thermal processes, we shall examine three main cases:

$$R_nM\ (gas) \rightleftarrows nR\ (gas) + M\ (gas), \quad (6)$$

$$R_nM\ (cond.) \rightleftarrows nR\ (cond.) + M\ (gas), \quad (7)$$

$$R_nM\ (gas) \rightleftarrows nR\ (gas) + M\ (solid), \quad (8)$$

where (gas), (cond.), and (solid) denote respectively the gas, condensed, and crystalline phases.

The homogeneous gas-phase process (6), under conditions where the states of the reactant obey the relations for ideal gases, is an analogue of the homopolar dissociation process (2), considered in its quantum-chemical aspect for the isolated states of the reactants. Because of this, the dissociation energies (D_n and $\bar{D}$) are identical with the dissociation enthalpy ΔH_D^0 for reaction (5). In describing the equilibrium in the decomposition reaction of polyatomic OMC molecules, one frequently employs the average enthalpy and entropy of dissociation of the metal–ligand bond. The results of the measurements of the energies and entropies of dissociation of the metal–organic ligand or radical bond have been discussed.[41-43,74-76]

Comparison of the enthalpy (ΔH) and entropy ($T\Delta S$) contributions to the Gibbs free energy (ΔG) of dissociation via reaction (6) for virtually all the known and investigated OMC[74] has shown that under standard conditions the contribution of the entropy term is only 5–30% of ΔH. Bearing in mind that the dissociation energies of all the bonds are positive[75] and that the entropy change on dissociation is likewise positive,[74] one may conclude that ΔG for all OMC dissociation processes in the gaseous state with formation of gaseous decomposition products and the metal vapour is always positive under standard conditions. Consequently almost all the OMC investigated hitherto are thermodynamically stable in relation to the gas-phase dissociation process at 298.15 K and a pressure of 1 atm. These conclusions confirm indirectly the results of extensive synthetic studies[24,25] during the last 10–15 years on the reactions of atomic (gaseous) metals with organic compounds when they are subjected to cocondensation at low temperatures.

With increase of temperature (at a constant pressure $p = 1$ atm), the contribution of the entropy term rises and at a specific temperature $T_{p,gas}$ the free energy ΔG of the dissociation reaction (6) becomes zero and then negative. Starting from this temperature, the OMC decomposition process becomes thermodynamically probable. The temperature $T_{p,gas}$ can be adopted as the temperature of the "onset" of the gas-phase OMC decomposition reaction characterising the thermal stability of the OMC in relation to the gas-phase decomposition reaction (6).

An estimate of the influence of pressure on the thermal stability of OMC has shown[21] that (1) at an elevated pressure the thermal thermodynamic stability of OMC is higher than at a reduced pressure; (2) the OMC thermal decomposition processes at a reduced pressure should occur at lower temperatures than at elevated pressures. These conclusions have been demonstrated qualitatively by known facts, namely that dibenzenetungsten(0) and dibenzenemolybdenum(0) decompose in a high vacuum at much lower temperatures than in a closed volume under the pressure of both decomposition products.[77,78]

Systematic studies have been made on the dependence of the dissociation energies[75] and dissociation entropies[74] of chemical bonds on the atomic numbers of the elements. It has been shown that the average dissociation energies $\bar{D}$ for compounds of non-transition elements within one Group in the Periodic System with carbon diminish with increase of the atomic number of the element, while for compounds of transition metals the opposite relation is observed: the average dissociation energy of the σ-bonds increases with increasing atomic number of the element down the Group.[75] This is also true of biscyclopentadienyl compounds, carbonyls, and other types of compounds of transition metals. On moving along the 3*d* series of transition metals, $\bar{D}$ diminishes with increasing atomic number of the element.[75,76] For the same non-transition element M in the analogous compounds, the values of D decrease in the following sequence as R is varied: Ar > Alk > Ph > Me > Et ≅ n-Pr ≅ n-Bu.[43]

The average M–C bond dissociation energies for non-transition elements reach a maximum on moving along the Period for Group IV elements.[43] The increase of $\bar{D}$(M–Alk) after the introduction of electron-accepting substituents into the OMC molecule, of the type $Alk_{n-m}MX_m$, where X = Cl, Br, I, or OH, compared with Alk_nM is of interest.[43] For the organobimetallic compounds $Alk_3M–MAlk_3$, the dissociation energies $\bar{D}$(M–Alk) are equal to those in Alk_4M; the metal–metal bond dissociation energies in compounds of the type $Alk_3M–MAlk_3$, which have been investigated, diminish in the sequence Si–Si > Ge–Ge > Sn–Sn,[43,76] while for the $M_{non\text{-}trans}–M_{trans}$ bonds [in compounds of the type $CpM_{trans}(CO)_3–M_{non\text{-}trans}Me_3$] the values of $\bar{D}$ lie in the sequence Cr–Ge < Cr–Sn < Mo–Ge < W–Ge < Mo–Sn < W–Sn, i.e. $\bar{D}$ increases with increasing atomic numbers of both metals, which is characteristic of transition metal OMC and not of non-transition metal OMC.

Analysis of the dependence of the average bond dissociation entropy on the position of the element in the Periodic System has shown[74,75] that $\Delta\bar{S}$(M–C) varies within much narrower limits than $\bar{D}$(M–C) and is in the range 15–45 cal mol^{-1} K^{-1}, the greatest number of values of $\Delta\bar{S}$ obtained lying in the range 30–40 cal mol^{-1} K^{-1}. Here $\Delta\bar{S}$(M–C) for the same Group of the Periodic System and isotypical compounds decreases with increasing atomic number, the effect being less pronounced for the heavier transition metals. The effect has been attributed[74,75] to the variation of the atomic radius of the metals in the Periodic System.

The $\Delta\bar{S}$(M–C) and $\bar{D}$(M–C) data can be used to calculate the average Gibbs free energies of dissociation of the bonds $\Delta\bar{G}$(M–C),[74] which may serve as a criterion of the stability of the OMC and the M–C bonds in them under standard conditions. The ΔG(M–C) for the OMC of non-transition and transition elements have been compared.[75,76]

Estimates of ΔG^0 [21,76,79] for the reactions

$$M\ (gas) + 2(C_5H_{5+n})\ (gas) \rightleftarrows (C_5H_5)_2M\ (gas) + nH_2\ (gas);$$

$$M{=}V,\ Cr,\ Mn,\ Fe,\ Co,\ Ni;\ n{=}0,\ 1,\ 3,\ 5.$$

$$Cr\ (gas) + 2(C_6H_6)\ (gas) \rightleftarrows (C_6H_6)_2Cr\ (gas).$$

show that the equilibrium in the gas-phase reactions with a

gaseous metal, involving synthesis and decomposition, is almost always displaced towards synthesis regardless of whether gas-phase radicals or stable organic compounds of the type of benzene or cyclopentadiene participate in the reaction. Although the entropy term contributes significantly to ΔG at elevated temperatues, the differences between the average M–C bond dissociation energies for different elements, the characteristic features of the variation of which were indicated above, should exhibit a marked influence.

On passing to heterogeneous OMC synthesis and decomposition processes (7) and (8), one should note the importance of considering the energy relations and the structures of the condensed phases of the reactants. If the condensed phase (crystal) has a molecular type of packing, then the contributions of ΔH and ΔS for the condensed phase of the OMC and the organic compounds, which occur in different parts of the reaction equation, partly cancel out and the position of the thermodynamic equilibrium in the synthesis-decomposition reaction involving the gaseous metal does not vary very markedly.[25,79] Specific features can be introduced only by intermolecular interactions in the condensed OMC phase additional to the van der Waals interactions. If the synthesis-decomposition reaction of the gaseous OMC with formation of gaseous organic decomposition products and the solid metal [Eqn.(8)] is considered, it is noted that the state of thermodynamic equilibrium in the reaction differs significantly from that for a purely gas-phase reaction. In the reaction involving the formation of the solid metal, for which this phase state is standard, the enthalpy of atomisation of the solid metal ΔH_f[M(gas)], i.e. the term which made a positive contribution to ΔG when the decomposition reaction was considered, giving rise to $\Delta G > 0$, virtually disappears and the state of equilibrium becomes markedly dependent on the enthalpy of formation of the decomposition products and on the entropy terms. Cases may be observed where $\Delta G > 0$ and $\Delta G < 0$, depending on ΔH_f[M)gas)] and other factors, for different OMC where the state of equilibrium of the gas-phase reaction is displaced towards synthesis.[21,25,79–81]

The radical change in the thermodynamic equilibrium and hence in the thermodynamic stability of OMC in the synthesis-decomposition reaction of dibenzenechromium(0) may be regarded as a classical example. While the equilibrium in the gas-phase reaction under standard conditions is displaced towards synthesis (see above), the equilibrium in the reaction involving the solid chromium phase is almost always displaced towards decomposition[21] under the same (standard) conditions:

$$(C_6H_6)_2Cr\ (gas) \rightleftarrows Cr\ (solid) + 2(C_6H_6)\ (gas).$$

Thus dibenzenechromium(0) is thermodynamically unstable in relation to the gas-phase decomposition with formation of solid metallic chromium. Such instability is manifested to an even greater extent for the bisarene derivatives of refractory metals, such as vanadium,[82] molybdenum,[77] tungsten,[78] titanium, niobium, and tantalum[83] as a consequence of the extremely high enthalpy of atomisation of the metals ΔH_f[M(gas)].

In the general case, for reactions involving the segregation of the solid metal, equilibrium should be attained at lower temperatures than for a purely gas-phase reaction.

For non-transition metals, for which the values of ΔH_f[M(gas)] are as a rule much lower, a shift of the equilibrium in the synthesis-decomposition reaction with participation of the solid metal towards synthesis is more likely,[80] as, for example, has been frequently observed for OMC of aluminium and certain other metals[81] and is also known from Paneth's classical studies on the reactions of free radicals with metallic mirrors.[15]

Thus the thermal thermodynamic stability of OMC is different for different decomposition reactions and is determined both by the thermodynamics of the OMC itself and by the phase state and the thermodynamic characteristics of the decomposition products.

In view of the foregoing, one may conclude that the thermodynamic stability of OMC in relation to the gas-phase decomposition process characterises, as it were, the possibility of the existence of the OMC in the gas phase (in the molecular form) and is thus close to the definition of the quantum-chemical stability, but refers solely to the set of OMC molecules in equilibrium with their decomposition products.

The thermodynamic stability of OMC in relation to the decomposition process with formation of the solid metal is more closely related to the definition of thermal stability in a real thermal decomposition process used to deposit coatings from the vapour phase and is more likely to characterise the reactivity of OMC than the possibility of the existence of OMC of the given type. The thermodynamic equilibrium between the solid metal and the gaseous OMC is attained more readily with increase of the surface area of the solid phase. It is noteworthy that the state of equilibrium for the solid metal and the condensed states of the OMC and the organic compound is likewise determined mainly by the high value of ΔH_f[M(gas)] and characterises the stability of the condensed state of the OMC in equilibrium with the solid metal. The majority of the OMC of refractory transition metals are thermodynamically unstable in these processes under standard conditions.[21,77–79,82] The thermodynamic instability of the OMC in relation to a specific decomposition process can be compensated by the kinetic stability and conversely, by virtue of the kinetic instability, in certain processes the thermodynamic stability may not be of decisive importance and the equilibrium (reversibility) of the process may be disturbed as a consequence of the operation of kinetic factors.

The transition from the gaseous to condensed (liquid or solid) states of the OMC is characterised by a significant change in the structure of the OMC. Apart from the molecular structure, the latter includes the relative disposition of the molecules, reflecting the intermolecular bonds (their packing).

Analogously to the way in which the molecular structure characterises the steric factor in electronic-nuclear interactions in the molecule, the structure of the condensed state of the OMC characterises the steric factor in the electronic-nuclear interactions in the set of molecules comprising the given states.

We shall consider the general types of the possible interactions between the OMC molecules in the condensed state: substituent (ligand)–substituent (ligand) (R ... R), substituent (ligand)–metal (R ... M), and metal–metal (M–M). The R ... R interactions are characteristic of organic chemistry, while the R ... M and M–M interactions constitute the specific features of the OMC.

The R ... R interactions are of the van der Waals type with energies up to 5 kcal mol^{-1}; their capacity for the formation of bonds is a maximum over a range of distances of ~2.5–3.5 Å.[84] These interactions determine the structure of molecular crystals.[84]

The intermolecular coordinate bonds with energies of ~3–10 kcal mol^{-1},[85] which lead to the formation of oligomeric and polymeric structures,[85–87] belong to the class of R ... M interactions. In the limit, these interactions can result in the formation of the R–M chemical bonds. This is confirmed, for example, by the oligomeric and polymeric structures of metal alkoxides or β-diketonates.[86]

The metal–metal interactions can also lead to the association of the molecules in the given state of aggregation. Thus many instances of the formation of infinite chains of OMC molecules and crystals with metal–metal bonds are known (see, for example, Ibers et al.[88]). The energy of these interactions is low compared with that of the M–M chemical bond (for example, the Rh–Rh bond energy is 18 kcal mol^{-1} [89]). The upper limit of the distances corresponding to the M–M chemical binding (~3–3.5 Å[88]) is comparable to the R ... R intermolecular contacts.

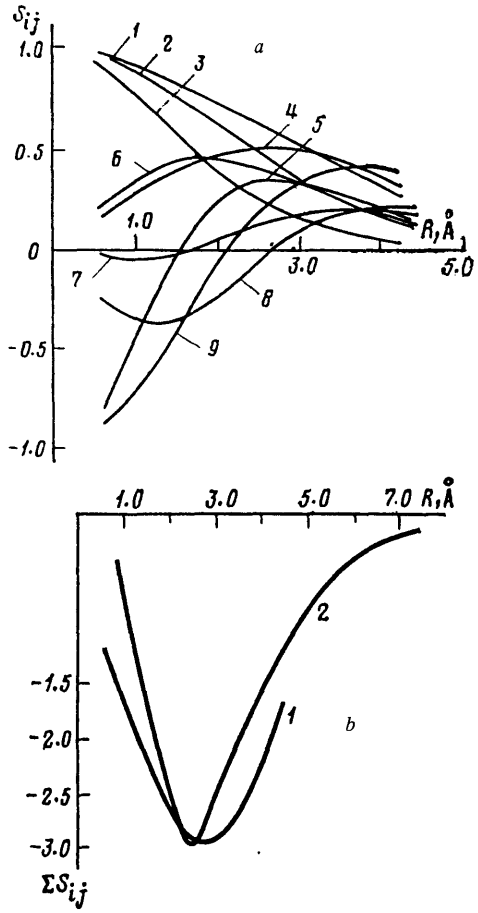

Figure 3. *a*) Dependence of the overlap integrals S_{ij} on the interatomic distance R in the Cr_2 molecule. The curves correspond to the following interactions: 1) 4*s*–4*s*; 2) $4p_\pi$–$4p_\pi$; 3) $3d_\sigma$–$3d_\sigma$; 4) 4*s*–4*p*; 5) $3d_\pi$–$3d_\pi$; 6) $3d_\pi$–$4p_\pi$; 7) $3d_\sigma$–4*s*; 8) $3d_\sigma$–$4p_\sigma$; 9) $4p_\sigma$–$4p_\sigma$; *b*) dependence of the sum ΣS_{ij} (curve *1*) and the potential of the Cr_2 molecule (curve *2*), calculated from experimental data in the form of the Morse potential, on the interatomic distance R in the Cr_2 molecule. Curves *1* and *2* have been normalised with respect to the minimum in curve *1*.

Analysis of the overlap integrals S_{ij} for the M–M bonds[90] has shown that for heavy metals the M–M interaction over distances of ~3–4 Å is still more intense and passes through a maximum for p_σ–p_σ, etc. Fig. 3 presents the values of S_{ij} based on the data of Batsanov and Zvyagina[90] and the semi-empirical Morse potential[91] for the Cr ... Cr interactions. In contrast to the "short range" Cr–C interaction, the Cr–Cr interactions are of the "long range" type and are characterised by a relatively broad minimum, which is due partly to a change in the contributions of different atomic orbitals of the metal.

All these factors confirm that it is legitimate to take into account the possibility of the formation of M–M bonds in considering the intermolecular interactions in OMC. The R ... R interactions have the character of boundary interactions and, in contrast to the R ... M and M–M interactions, are obligatory constituent elements of the intermolecular interactions in the condensed state of OMC.

On the basis of the foregoing, it is possible to trace the influence of the structure on the stability of the condensed state of OMC in relation to synthesis-decomposition processes, important for OMC and characteristic of such compounds, such as the formation of polynuclear OMC, metal clusters, and the solid metal from mononuclear OMC.

An estimate of the thermodynamic stability of the structure of the condensed state of OMC in relation to the formation in the latter of M–M bonds (apart from the intermolecular R ... R bonds) represents in essence an estimate of the stability of the structure of mononuclear OMC in relation to the formation of polynuclear OMC containing metal–metal bonds.

We shall estimate the contributions of the enthalpy and entropy terms to the ΔG of the transition from the structure of the OMC with intermolecular R ... R bonds to the structure with intermolecular R ... R and M–M bonds.

The enthalpy of the process consists of the changes in ΔH corresponding to the formation of M–M bonds and to the modification under these conditions of the intermolecular and intramolecular R ... R interactions. Overall, the intermolecular M–M interactions are energetically more favourable than the R ... R interactions. Consequently, in the absence of hindrance to the formation of M–M bonds by the R ... R interactions, the thermodynamic equilibrium is displaced towards the formation of the OMC structure with M–M bonds. The intermolecular (intramolecular) repulsion, which increases rapidly with decrease of the R...R distances, exerts the opposite influence and can render the formation of M–M bonds thermodynamically impossible.

The entropy term hinders the formation of M–M bonds, because the entropy of the system falls when they are formed ($\Delta S < 0$). ΔS depends directly on the steric hindrance to the formation of M–M bonds both by the molecular structure of the OMC and by the molecular packing: the greater the hindrance, the higher the value of ΔS.

Thus the structure of the condensed state of the OMC with intermolecular R...R bonds is more stable in relation to the OMC structure with intermolecular R...R and M–M bonds the greater the steric hindrance to the formation of these bonds by the intermolecular or intramolecular R...R interactions, in particular the higher the degree of shielding of the metal atom or the active centres in the substituents (ligands). Consequently, by creating a hindrance due to intramolecular and intermolecular non-bonding interactions, it is possible to achieve the stabilisation of the structure with R...R bonds relative to the formation of M–M bonds in the latter.

IV. KINETIC STABILITY

Since all real processes take place over a period of time, a significant factor determining the stability of OMC is the kinetics of the synthesis-decomposition reactions, the

principal features of which constitute the foundations of the concept of the kinetic stability and instability of OMC. Analogously to the previous two aspects of the consideration of the stability of OMC, the kinetic stability is determined for different processes involving perturbations in the state of equilibrium (the synthesis-decomposition of OMC). Under the conditions of the thermal processes (6)–(8), the kinetic stabiiity is one of the important components which determine the thermal stability of the OMC.

In order to determine the principal characteristics of the thermal kinetic stability of OMC, we shall consider the features of the gas-phase OMC synthesis-decomposition reaction:

$$R_nM \rightleftarrows R_{n-1}M + R \rightleftarrows R_{n-2}M + 2R \rightleftarrows \ldots \rightleftarrows M + nR.$$

Assuming that each of the consecutive stages presented above can determine the overall rate, consideration of the case where $n = 1$ or of the overall process

$$R_nM \rightleftarrows nR + M.$$

will not be an unduly drastic simplification. For $n = 1$, the process reduces to the dissociation reaction of diatomic molecules and the recombination of two atoms (or radicals), which have been thoroughly described in the literature.[92–95]

It is known from the theory of absolute reaction rates[96,97] that the intermediate activated state in the forward dissociation reaction and in the reverse recombination reaction is the same:

$$R{-}M \underset{k_2}{\overset{k_1}{\rightleftarrows}} [R{-}M]^{\neq} \rightleftarrows R + M.$$

However, the rates of the forward and reverse reactions can differ appreciably.

The forward dissociation reaction is a unimolecular process,[92] while the reverse reaction is a bimolecular process. The rate of the unimolecular dissociation reaction of RM may be determined by the rates of its two stages: (1) the activation process with formation of the intermediate activated state $[R{-}M]^{\neq}$ and (2) the transition of the activated state $[R{-}M]^{\neq}$ through the barrier with formation of the decomposition products.[96,97]

When equilibrium thermodynamics is used in the activated complex theory for the determination of the decomposition reaction rate constant, the latter is given by the following expression (the Arrhenius law):[92,93,96,97]

$$k = \varkappa \frac{kT}{h} e^{-\Delta G^{\neq}/RT} = \varkappa \frac{kT}{h} e^{\Delta S^{\neq}/R} \cdot e^{-\Delta H^{\neq}/RT},$$

where $\Delta G^{\neq}$, $\Delta S^{\neq}$, and $\Delta H^{\neq}$ are respectively the changes in the Gibbs free energy, entropy, and enthalpy of activation.

According to Moin,[98] $\Delta H^{\neq}$ is determined as the difference between the sums of the dissociation energies of the bonds being ruptured ΣD_r and the dissociation energies of the activated bonds $\Sigma D^{\neq}$:

$$\Delta H^{\neq} = \Sigma D_r - \Sigma D^{\neq}.$$

The factor kT/h characterises the frequencies of the collisions of the molecules during activation and increases with increase of temperature and pressure in gas-phase reactions.

The factor $e^{\Delta S^{\neq}/R}$ characterises the efficiency of the molecular collisions leading to reaction (the probability factor). The activation entropy $\Delta S^{\neq}$ then depends on the redistribution of energy between the different degrees of freedom in the activated state and is determined by the symmetry, i.e. by the steric structure of the OMC.

These kinetic features are valid both for the forward decomposition reaction and for the reverse synthesis reaction (recombination). The difference between the rates of the forward and reverse reactions is caused by the differences in the frequency and probability factors and in $\Delta H^{\neq}$. The kinetic conditions for the OMC thermal decomposition reactions and the reverse synthetic reactions have therefore proved to be such that the rate of one of the reactions is higher or lower than the other by any orders of magnitude.

The low overall OMC pressures *in vacuo* of the low OMC partial pressures in the carrier gas, used in carrying out the OMC thermal decomposition process, favour thermal decomposition at a higher rate and conversely they hinder the reverse synthetic reaction, which is significant only at high pressures, where the probabilities of binary and ternary collisions become appreciable.

Nevertheless the kinetic instability of OMC in the gas phase determined above is not decisive under the usual conditions at low temperatures where the rates of decomposition of OMC are low. Therefore, even in the presence of the solid metal, when the OMC may be thermodynamically unstable, as happens, for example, in the case of dibenzenechromium(0),[79] the OMC possesses kinetic stability as a consequence of the low rates of its decomposition; in other words, under these conditions the thermodynamic equilibrium is not established because of kinetic limitations. On the other hand, with increase of temperature the reaction rates also increase, which leads both to the rapid attainment of a state which is thermodynamically stable under the given conditions and to the manifestation of the kinetic instability of the OMC. These features can be clearly seen in relation to the synthesis-decomposition reactions of dibenzenechromium(0).[21,79]

Despite the thermodynamic stability of dibenzenechromium(0) in relation to the gas-phase decomposition reaction, it is kinetically unstable in the gas phase reaction because the forward decomposition reaction is a unimolecular process, while the synthetic reaction is a termolecular process or consists of two consecutive bimolecular processes, whose probability is low at reduced pressure compared with that of the unimolecular process. Since the rate of the forward gas-phase decomposition reaction of dibenzenechromium(0) should be much higher than the rate of the reverse synthetic reaction, an appreciable concentration of chromium atoms is established in the system. In view of the higher probability of a binary collision than a ternary collision, atomic chromium may recombine in binary collisions. If there is a possibility of removing the Cr–Cr bond energy to a third species or to the wall (support), the equilibrium in the recombination reaction shifts towards the formation of metallic clusters and ultimately of the solid metallic phase. Thus the kinetic conditions in the forward and reverse reactions may promote a shift of the reaction equilibrium to a thermodynamically unstable state—towards decomposition in the gas-phase reaction.

The appearance of the nuclei of metallic clusters and the solid phase during the process modifies the gas-phase reaction, so that the latter becomes a reaction with formation of the solid metal for which the fundamentally stable state is a dissociative state (decomposition).

Analysis of the conditions for the kinetic stability of gaseous substances and in particular of the OMC has shown that the stability increases with decrease of temperature and increase of pressure in the OMC $\rightleftarrows$ decomposition product system.[21]

From the standpoint of the influence of the structure on the kinetic stability of OMC, it is interesting to examine the effect of structure on the individual factors influencing the reaction rate constant. The factor kT/h is independent of the nature of the reactants and the activated state;[97] virtually the entire structural "load" is carried by the entropy (probability) factor $e^{\Delta S^{\neq}/R}$. If the structure of

the intermediate activated state differs little from that of the initial molecules, $\Delta S^{\neq}$ is low and the reaction rate falls. When the structure of the intermediate activated state of the complex is close to that of the decomposition products, $\Delta S^{\neq}$ is almost equal to the entropy of reaction ΔS and may be large and positive. If the intermediate activated state or the final products have a greater number of bonds than the initial reactants, $\Delta S^{\neq}$ may be negative, which diminishes the pre-exponential factor, although the formation of new bonds entails a decrease of the activation energy for the reaction (isokinetic law). Overall, the following statement may be made concerning the influence of structure on the entropy factor in the OMC thermal decomposition rate constant: the greater the rearrangement of the structure of the initial OMC in the intermediate activated state and the closer it is to that of the final products, the higher the decomposition reaction rate constant and the lower the kinetic stability of the OMC. Virtually no systematic estimates of $\Delta S^{\neq}$ for the OMC thermal decomposition reactions exist as yet; one can only point to a few investigations.[20,21]

The problem of the kinetic stability of OMC involves yet another important question, namely that of the efficiency of the activation energy transfer to the bond being ruptured, which depends on the distribution and the possibilities for the redistribution of the activation energy among the electronic, vibrational, and rotational degrees of freedom of the OMC molecule. The structure of the OMC may play a dual role in the redistribution of energy among the degrees of freedom and in its localisation in one of the stretching vibrations. If the OMC contain groups and fragments whose vibrations and rotations are of the type of symmetric or asymmetric tops, which interact strongly with other molecular vibrations, in particular, with the stretching vibrations responsible for the dissociation process, then in these molecules the activation energy is readily localised precisely in such torsional vibrations or rotations of the fragments and the probability of its localisation in the stretching vibration should be lower than in the molecules where such possibilities are absent.

Substituents and ligands of this type are, for example, the neopentyl (CH_2CMe_3), trimethylsilyl ($SiMe_3$), trimethylsilylmethyl (CH_2SiMe_3), benzyl (CH_2Ph), diphenylmethyl ($CHPh_2$), triphenylmethyl (CPh_3), adamantyl, cyclohexyl, norbornyl, cyanomethyl (CH_2CN), polychloromethyl ($CH_{3-n}Cl_n$), perfluoroalkyl (for example, CF_3), and other groups as well as ligands: $:C{\rightleftarrows}O$, $:PF_3$, and $:P(OR)_3$, where R = methyl, ethyl, phenyl, *o*-biphenylyl, etc.

Apart from their fairly high efficiency in delocalising the activation energy over the molecule, such substituents and ligands are able to shield the reaction centre, i.e. the metal–substituent (ligand) bond, from direct activation by virtue of their steric structure. The transmission of activation via the above groups to this bond is relatively ineffective as a consequence of the presence of a large number of high-energy vibrations in these fragments compared with the low-frequency stretching vibrations of the metal–substituent (ligand) bond and owing to the absence of the possibility of complex formation for the substituent. Such complex formation is possible for substituents of the type of allyl, alkynyl, and others as a consequence of a "viscous" ["non-elastic" (Editor of Translation)] collision with the multiple bond or collisions of substituted groups with hydroxy-, amino-, and other groups active in the formation of hydrogen bonds.

The steric shielding by the above substituents (ligands) of the central metal atom is such that the OMC molecule constitutes, as it were, an elastic sphere which is difficult to deform by compression and extension. Bearing in mind the chemical inertness of such substituents (ligands) in relation to both similar reagents and functional reagents, it is possible to account for the appreciable kinetic stability of OMC of this kind. A large number of kinetically stable OMC with substituents and ligands of the sort described have been obtained by Wilkinson and other workers.[13,14]

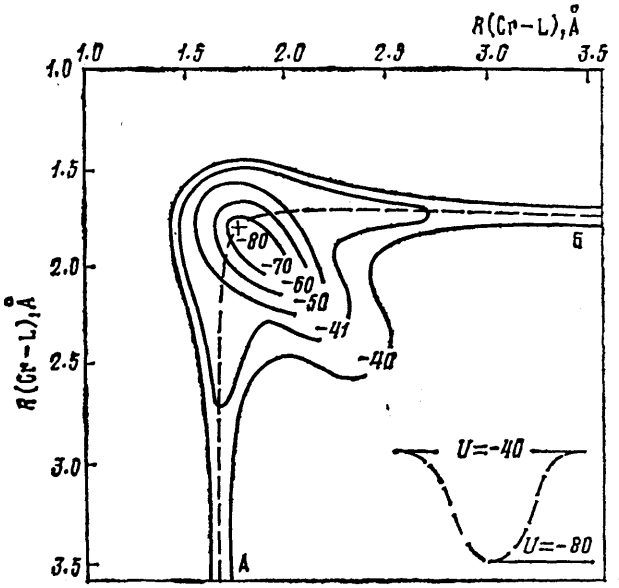

Figure 4. The potential energy surface for linear $(\eta^6\text{-L})_2Cr$ molecules, where L = C_6R_6 and R = H or Me.[61] States of the molecular fragments $(L^{(2)}\text{–Cr}\ldots L^{(1)}$ and $L^{(2)}\ldots\text{Cr–}L^{(1)})$ correspond to points A and B and the sign ± denotes the minimum in the potential well.

The set of energy and steric factors reflecting the kinetic stability or instability of OMC in a gas-phase process is in its turn reflected in the multidimensional potential energy surface for the OMC molecule. Fig. 4 illustrates the PES for dibenzenechromium(0),[61] which is characteristic also of other molecules of the type L_2M (L = ligand). The minimum in the potential well corresponds to a thermodynamically and kinetically stable state. Acquisition of an activation energy $E_a \geq D_1$ (D_1 is the energy of the abstraction of the first group L from the Cr atom) by the dibenzenechromium molecules induces movement along the reaction coordinate $Cr\text{–}L^{(1)}$ corresponding to the stepwise dissociation: $L^{(2)}\text{–Cr–}L^{(1)} \rightarrow L^{(2)}\text{–Cr} + L^{(1)}$. The activation energy in the unimolecular process is then virtually close to the dissociation energy D_1 of the first bond. Movement along the reaction coordinate $Cr\text{–}L^{(2)}$ arises similarly. After this, thermal activation takes place and the L–Cr fragment decomposes. For high levels of thermal excitation, following the absorption of light quanta or electron impact, there is a possibility of the transfer to the molecule of the energy $E_a \geq D_1 + D_2 = 2\bar{D}$. In this case there is a possibility of a concerted decomposition with the simultaneous dissociation of two ligands (movement

along the PES diagonal). This kind of decomposition of OMC is almost always observed when $D_2 < D_1$ and when $E_a \geq D_1$. The abstraction of a second ligand is greatly accelerated and takes place almost simultaneously with the first abstraction step (because $E_a \gg D_2$). A decomposition of this type has been observed for R_2Hg [99] and certain other OMC.

As in the consideration of the thermodynamic stability of OMC, we shall estimate the role of intramolecular and intermolecular non-bonding interactions in ensuring the kinetic stability of the condensed state of OMC relative to the formation of M–M bonds in the latter. The magnitude and sign of $\Delta H^{\neq}$ and hence also the rate of the process are determined by the relative contributions of opposite tendencies: the endeavour by the OMC to realise a state with M–M bonds (because this is favoured by thermodynamic factors) and the obstacle to this attempt by the M–R bonds and the non-bonding R...R interactions in the molecule and in the packing of the OMC.

The contribution of the entropy term retards the formation of M–M bonds, because the entropy change corresponding to this is negative. On the other hand, any change in the structure of the OMC involving a weakening and rupture of the M–R bonds is reflected in a positive contribution to $\Delta S^{\neq}$ (because the entropy then increases), which accelearates the process. Such structural changes are linked directly to the "rigidity" or "looseness" of both the molecular structure and of the packing of the OMC molecules. The more "rigid" molecules and molecular packing are kinetically more stable in relation to the formation of M–M bonds in the condensed state. The obstacles offered to the formation of M–M bonds in the condensed state of the OMC by the non-bonding R...R interactions and the "rigidity" or "looseness" of the structure are directly linked to the degree of steric shielding of the metal atoms from one another by the substituents (ligands), determined both by the molecular structure and by the molecular packing.

The symmetry (or, in other words, the degree of order) in the structure of the condensed state of the OMC plays an important role in such shielding. Since the character of the molecular collisions in the liquid (partial ordering) is such that their number is sufficient for the realisation of mutual orientations of the molecules which promote the formation of M–M bonds in the activated complex, one may conclude that in this case the steric hindrance to the formation of these bonds is generated mainly due to the shielding of the metal atom in the OMC molecular structure. In the crystalline state (total order) the possibility of the formation of M–M bonds is influenced also by the crystal packing. For example, the compound $(Ph_3Ge)_2Hg$ decomposes with liberation of metallic mercury in solution, on fusion, and also in the amorphous solid state, but is stable in the crystalline state, because the crystal packing of the molecules ensures the complete shielding of the Hg atoms from one another.[100]

Thus one may reach the following conclusion: the greater the steric shielding of the metal atoms from one another in the structure of the condensed state of the OMC (owing to its molecular structure or molecular packing), the more stable is this OMC state in the thermodynamic and kinetic aspect in relation to the formation of polynuclear OMC, metal clusters, and the solid metal, i.e. products containing metal–metal bonds.

The characteristic feature of the relation between the structure of the condensed state of the OMC and its stability in relation to the formation of M–M bonds described above is valid not only for mononuclear OMC of the type of MR_n but also for polynuclear OMC, namely metal clusters having the composition M_nR_m, because their molecules have in principle a structure analogous to that of the mononuclear OMC with the sole difference that in them not one atom but a group of metal atoms is surrounded by substituents (ligands). It is valid also for the characterisation of the stability of the condensed state of the OMC relative to the formation in the latter of intermolecular M...R bonds, i.e. the formation of oligomeric and polymeric structures.

V. THE STABILITY OF ORGANOMETALLIC COMPOUNDS UNDER NON-EQUILIBRIUM CONDITIONS

In most cases organometallic compounds exist in their synthetic and decomposition processes under the conditions of uncompensated energy (heat, radiation) and mass (changes in the relative amounts of the OMC and organic compounds—products resulting from decomposition and the segregation of the solid metal) fluxes. The presence of such fluxes disturbs the adiabatic conditions and leads to a non-equilibrium state of the system and to irreversible processes. Typical examples of such irreversible processes under non-equilibrium conditions include (1) the cryosynthesis of OMC with atomic (gaseous) metals,[24,25] (2) the deposition of the metal from the OMC vapour phase during thermal decomposition,[20,21] (3) the photodecomposition of OMC in the condensed or gaseous phase,[16,18] (4) the decomposition and synthesis of OMC under the influence of electron impact *in vacuo* or in a gas,[28,29] and a number of others.

The cryosynthesis of OMC with gaseous metals is an irreversible process by virtue of the very formulation of the experiment, because the latter employs extremely high supersaturations of the vapour phase with respect to the metal. The metal vapour obtained at high temperatures (~2000 to 2500 K) in a form in equilibrium with the condensed phase, is transported *in vacuo* as a flux of atoms which react at low temperatures with the condensed phase of the organic compound. At low temperatures the metal vapour is then in a state remote from equilibrium and the cryosynthesis of the OMC is therefore significantly irreversible.

The deposition of the metal from the vapour phase of the OMC during thermal decomposition[20,21] is carried out under the conditions of an energy (heat) flux through the support to the OMC and mass fluxes [of the OMC to the support and of organic compounds (decomposition products) from the support, condensed phase of the metal being deposited on the support]. The optimum conditions for the deposition process are then believed to be a flux of OMC unlimited with respect to time and an energy flux from the side of the support "unlimited with respect to power" and time.[20] Such conditions render the deposition process irreversible.

In the OMC decomposition processes under the influence of electromagnetic radiation (photodecomposition) or electron impact the distribution of the molecules with respect to energy differs from the equilibrium distribution and the decomposition products are frequently formed in electronically excited states[16,23,29] as a result of which these processes are likewise irreversible.

The kinetics of the irreversible processes under non-equilibrium conditions depend on how far the state of the system deviates from equilibrium. Near equilibrium, the rate of the process is usually linearly related to the process parameters and the method of stationary concentrations can be used for its description. Under conditions remote from thermodynamic equilibrium, non-linear relations are observed and are responsible for the presence of many different stationary states of the system and the occurrence of autowave processes and decaying vibrations in homogeneous gas-phase and liquid-phase reactions and in heterogeneous gas–solid and liquid solution–solid reactions.[101–106]

Apart from chemical kinetic factors, the study of non-equilibrium kinetics of irreversible processes[107] includes the consideration of mass-transfer (diffusion, turbulence) and heat transfer (thermal conductivity, convection) factors, small and large fluctuations in the state of the system, and also non-equilibrium states and irreversible processes in the interaction of the molecules with the electromagnetic radiation. The stability or instability of the system, in particular, of the OMC + decomposition products system, under such conditions, which approach those which obtain in reality, is determined by methods based on the theory of non-linear vibrations,[108] the non-equilibrium thermodynamics of irreversible processes,[101-104] synergistic relations,[109] or catastrophe theory.[106,110]

The OMC synthesis-decomposition processes occurring under conditions close to equilibrium should, generally speaking, lead to the decomposition of the structure,[101] while under conditions remote from equilibrium there is a possibility that the formation of dissipative structures may be observed. It is known[101] that chemical instabilities, which disturb the symmetry of the system, lead to the spontaneous self-organisation of spatial order in the system with formation of dissipative structures.[101-105]

The instability which leads to the disturbance of the symmetry in the arrangement of atoms or electrons is observed both in isolated molecules of OMC and coordination compounds (the Jahn–Teller effect[30]) and in solids (the charge-orbital ordering in the structure of the solid,[111] Peierls instability of M_n chains,[112] etc.).

The formation of metastable and high-temperature phases of the metal in the thermal decomposition of OMC,[21] the appearance of electronically excited states of the metal atoms and singly-charged metal ions on decomposition under electron impact (on the basis of emission spectra[29]) and on photo-decomposition or decomposition induced by a laser (on the basis of absorption[16] and emission[23] spectra), and the segregation of the metal under the conditions of the low-temperature decomposition of the OMC, in particular bistriphenylgermylmercury, on cooling the solution to 77 K[113] are evidence for the thermodynamic non-equilibrium state of the OMC + decomposition product system.

If the state of the OMC is thermodynamically stable (or chemically stable according to Gray[114]) and stable with respect to diffusion,[114] one can assume that such a state is stable as regards all aspects of stability (quantum-chemical, thermodynamic, kinetic, and macrokinetic) and is an equilibrium state. Chemical instability can never be observed in an equilibrium system but it can play an indirect role under conditions remote from equilibrium. The region of the phase space in which chemical instabilities can be observed is then always located near a region where diffusion instabilities exist.[114] The diffusion stability of an atomic metal + organic complex-forming compound system gives rise to the possibility, in the course of matrix synthesis, of the transition of the system to a kinetically and thermodynamically stable state of the OMC as a result of fluctuations. On the other hand, the diffusion instability of such a system leads to the thermodynamic instability of the OMC as a consequence of its kinetic instability, because of the possibility that the metal atoms may aggregate and an equilibrium may be established between the OMC and the solid metal or metal clusters having a large effective surface area.[25,80] Rigid or highly viscous matrices are therefore used for the synthesis of OMC with atomic metals. The breakdown of conditions for the matrix isolation of the metal atoms from one another and the diffusion instability of the matrix[24,115] lead to a greater probability of the formation of polynuclear OMC and metal clusters as products of the condensation of the intermediate compounds, in which the number of ligands at the metal is insufficient for the kinetic stabilisation of the OMC: $M + L \rightarrow ML \xrightarrow{ML} M_2L_2$ and $M + ML_2 \rightarrow M_2L_2$, etc. Reactions of bistoluenechromium(0) and bistoluenevanadium(0) of a similar type with chromium and vanadium atoms have been recently discovered.[116]

A good example of the formation of dissipative structures is provided by the irreversible heterogeneous gas–solid reactions used for the deposition of inorganic coatings from the vapour phase in the thermal decomposition of OMC.[20,21] The growing surface of the solid phase can be regarded as an open thermodynamic system in deposition processes.[117] The characteristic features of the formation of dissipative structures in these processes have been investigated in fair detail in a number of studies.[20,21,117-123] It has been shown that processes involving the formation of a solid phase (the attainment of stationary surface areas of the growing solid phase, the multiphase nature of the deposit, the aggregation of particles and their dynamic characteristics, and the layer structure of the particles formed in the kinetic region of the reaction),[117] OMC adsorption processes and processes involving the desorption of the decomposition products,[21] the possible autocatalytic processes,[118] the finite rate of removal of the decomposition products,[120] the limited thermal conductivity of the support, and the inadequate power of the heat flux through the support[121] play an important role in their formation. Vibrational and monotonic processes involving the attainment of stationary states,[119] the limitation of the rate of the deposition process with respect to pressure and the occurrence of a peak in this rate,[119] temperature hysteresis and the excitation of auto-oscillations in the rate of deposition,[121] the fixation of time oscillations in concentration and temperature in the form of three-dimensional layer structures of the coatings,[119,122,123] and also the fixation of three-dimensional fluctuations of the rate of growth in the form of columnar structures[21,123,124] and filamental crystals[21,125] have been observed experimentally. Studies of theoretical models of the deposition process have demonstrated their satisfactory agreement with experiment.[21]

The formation of dissipative structures in a solution of an OMC has been observed for allylpalladium compounds[126] under the conditions of hindered diffusion in Liesegang rings and also for the ferrocene–ferrocenium system on irradiation with visible light of their solutions in alcohols.[127]

Under the conditions of non-linear kinetics, there is a possibility of a state of the system such that the OMC decomposition process is strongly retarded, despite the existence of conditions under which the OMC might have been unstable both thermodynamically (according to equilibrium thermodynamics) and kinetically. In such cases the non-equilibrium thermodynamic stability of the OMC in relation to the decomposition process arises, but this stability corresponds to the attainment by the system of a stationary state which in the general case may be unstable in time (in relation to local structural fluctuations). This state may be called a dynamically stable non-equilibrium state, which corresponds to a definite degree of the thermal decomposition process.

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Thus one may conclude that a complex and varied problem such as that of the stability of OMC in their synthetic and decomposition processes must be solved only by a combined procedure on the basis of general concepts of the stability and structure of material systems taking into account all its aspects and the energy and steric factors. This approach makes it possible to investigate the stability of various types of OMC in relation to perturbations of any type, to reduce to

an integral unique system the results obtained in this field, and to discover various aspects of the problem and their interrelation. The approach can also help to abolish the existing confusion among investigators who mix up various aspects of the stability of OMC. On the other hand, the combined approach is very fruitful, because it allows one to use for the solution of the problem the advances in various sciences—chemistry, physics, and mathematics. It must be emphasised that the approach described permits the investigation of the OMC synthesis-decomposition processes, starting with idealised processes in an isolated OMC molecule and continuing up to real processes, which constitute the basis of a series of new promising technologies involving the industrial application of OMC.[20,21,24,25]

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Thermal Decomposition and Stabilisation of Poly(vinyl Chloride)

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The kinetics and mechanism of the thermal dehydrochlorination of poly(vinyl chloride) and low-molecular-weight chlorohydrocarbons which model various fragments of the polymer molecule, are discussed. Studies designed to determine the qualitative and quantitative compositions of the unstable fragments in poly(vinyl chloride) macromolecules by ^{13}C NMR are examined. Attention is concentrated on the consideration of the mechanism of the action of the most effective thermostabilisers for the polymer-organotin compounds. The principal features of synergism in the stabilisation of poly(vinyl chloride) and the mechanism of the action of synergistic mixtures are analysed.
The bibliography includes 107 references.

CONTENTS

I. Introduction 755
II. Thermal decomposition of low-molecular-weight model compounds 755
III. Kinetics of the thermal decomposition of poly(vinyl chloride) 756
IV. The nature of the unstable fragments in poly(vinyl chloride) macromolecules 758
V. The mechanism of the thermal decomposition of poly(vinyl chloride) in the absence of HCl 760
VI. The mechanism of the autocatalytic decomposition of the polymer 760
VII. The mechanism of the action of effective stabilisers of poly(vinyl chloride) in its thermal decomposition 761

I. INTRODUCTION

Poly(vinyl chloride) (PVC) occupies one of the leading places in the world manufacture of polymeric materials. An important disadvantage of PVC is its instability towards various kinds of thermal and chemical influences. The thermal ageing of the polymer begins above 373 K.

The main principles of the ageing and stabilisation of polymers have been examined in Emanuel' and Buchachenko's book.[1] Various aspects of the problem of the thermal decomposition and stabilisation of PVC have been the centre of attention of many investigators. Studies on the ageing and stabilisation of PVC in Gorky are being pursued under the supervision of G.A.Razuvaev.

The aim of the present review is to analyse the present state of research into the main problems of the thermal decomposition and stabilisation of PVC. PVC belongs to the class of polymers which decompose under the influence of heat with elimination of side fragments from the macromolecules with the preferential formation of one low-molecular-weight product (namely HCl—more than 90%) and polyenes:

$$\sim(CH_2—CHCl)_n\sim \rightarrow mHCl + \sim(CH_2—CHCl)_{n-m}—(CH=CH)_m\sim;\quad n > m.$$

Despite the apparent simplicity of this overall reaction, investigators of the thermal decomposition of PVC have encountered extremely complex processes, some of the details of which still remain obscure.

II. THERMAL DECOMPOSITION OF LOW-MOLECULAR-WEIGHT MODEL COMPOUNDS

The experimental data (Table 1) on the thermal decomposition of compounds modelling various fragments of PVC macromolecules permit the following conclusions. In gaseous and liquid phases all chlorohydrocarbons decompose under the influence of heat with formation of HCl and an olefin (other products have not been detected). The kinetic curves for the decomposition of chlorohydrocarbons are described by first-order equations. In terms of the rate of their decomposition (or in terms of the corresponding rate constants), alkyl chlorides can be arranged in the sequence tertiary ≫ secondary ≫ primary.

Table 1. Arrhenius parameters and the temperature ranges of the thermal decomposition reactions of low-molecular-weight models of fragments of PVC macromolecules.

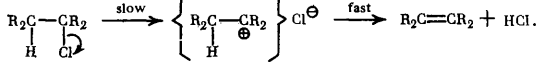
Model compound	$\lg A$, s^{-1}	E, kJ mol^{-1}	ΔT*, K	Phase	Refs.
Propyl chloride	13.45	230	693—751	gas	[2]
Pentyl chloride	13.80	232	683—723	»	[3]
s-Butyl chloride	13.75	210	612—663	»	[2]
t-Butyl chloride	12.40	173	563—614	»	[4]
3-Chlorobut-1-ene	13.34	203	593—683	»	[5]
4-Chlorohex-2-ene	10.75	142	523—586	»	[6]
6-Chlorohepta-2,4-diene	10.43	145	575—620	»	[7]
2-Chloro-2-methoxyethyl	11.46	140	453—523	»	[8]
8-Chlorohexadecane	10.55	151	509—557	liquid	[9]
8-Chloro-6-tridecylene	8.14	105	438—469	»	[9]
7-Chlorononа-3,5-diene	7.99	81	343—369	»	[9]

*ΔT = temperature range of the decomposition reaction.

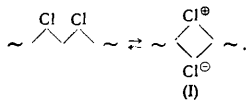
The activation energy for the thermal decomposition of secondary derivatives is lower by 21—33.5 kJ mol^{-1} and that of tertiary degrees is lower by 29—33.5 kJ mol^{-1} than the activation energy for the decomposition of primary derivatives. The reaction is greatly accelerated by the presence of a non-terminal double bond in the β-position relative to the chlorine atom. If the carbon—carbon bond is located at the end of the molecule (as in 3-chlorobut-1-ene), then the activation energy for the thermal decomposition of this compound is much higher than for a compound with an internal double bond (as in 4-chlorohex-2-ene) and is only slightly lower than the activation energy for the thermal decomposition of secondary-chlorohydrocarbons. An alkoxy-group

in the α-position relative to the chlorine has an appreciable accelerating effect on the thermal decomposition of the chlorohydrocarbon (Table 1).

There is no rigorous evidence in the literature concerning the elementary steps in the thermal dehydrochlorination of the chlorohydrocarbons presented in Table 1. The absence of compounds other than HCl and an olefin, the absence of an appreciable retarding effect by free radical inhibitors on the thermal decomposition of the chlorohydrocarbons listed in Table 1, a marked accelerating effect of nucleophilic substituents (groups with a carbon–carbon double bond and alkyl and alkoxy-groups in the α-position relative to the carbon–carbon bond), and the acceleration of the thermal decomposition of chlorohydrocarbons in the liquid phase with increase of the polarity and basicity of the solvent have been established experimentally.[2–10] All these factors suggested[2,8] that the thermal decomposition reactions of chlorohydrocarbons are two-stage processes of type E1 (unimolecular elimination reactions) and that the first and rate-determining stage is an intense polarisation (partial ionisation but not dissociation) of the C–Cl bond:



It has been recently suggested[11] that the primary elementary step in the thermal dehydrochlorination of chlorohydrocarbons which model the PVC molecule is the formation of cyclic chloronium ions:



(I)

It has been shown[11,12] that a large amount of olefin (~30%) and HCl is formed in the liquid phase during the thermal decomposition of a chlorohydrocarbon containing in its molecule one chlorine atom (7-chlorotridecane) in the presence of dodecane-1-thiol or 9,10-dihydroanthracene. The thermal decomposition of chlorohydrocarbons containing two or three chlorine atoms per molecule (4,6-dichloro-n-nonane, 2,4,6-trichloro-n-heptane) in the presence of the same chain transfer agents yields only the chlorohydrocarbon reduction product. Thus different products are formed from monochlorohydrocarbons, on the one hand, and from dichloro- and trichlorohydrocarbons, on the other.

It has been shown[11,12] that the thermal decomposition of polychlorohydrocarbons, modelling the fragments of PVC macromolecules, in the presence of thiols involves the reaction

$$\sim CH_2{-}CHCl\sim + 2RSH \rightarrow \sim CH_2{-}CH_2\sim + RSSR + HCl; \quad R = Alk, Ar. \qquad (1)$$

The composition of the reaction products, in particular the presence of a disulphide, indicates a free-radical process mechanism.

Depending on the reaction conditions, the cyclic chloronium ion (I) can decompose both via a free-radical mechanism (in the presence of an electron donor and an effective chain transfer agent) and via an ionic-molecular mechansim.[11] There is also a possibility of a radical-chain mechanism of the thermal decomposition of polychlorohydrocarbons in the presence of active chain transfer agents, which include thiols and 9,10-dihydroanthracene.

The effective activation energy for a radical chain reaction with quadratic chain termination is described by the expression[12]

$$E_{eff} = \tfrac{1}{2}E_i + E_p - \tfrac{1}{2}E_t,$$

where E_i is the activation energy for the initiation step (approximately equal to the energy of the C–Cl bond dissociated), E_p the activation energy for the most endothermic chain propagation stage, and E_t the activation energy for chain termination. E_i and E_p make the greatest contribution to E_{eff}.

The C–Cl bond energy ($\sim E_i$) in chlorohydrocarbons having the structure $\sim(CH_2 - CHCl)_n\sim$ is 326.6 kJ mol^{-1}, while in compounds of the type $\sim(CH{=}CH)_m{-}CHCl\sim$ it amounts to 234.5–251.2 kJ mol^{-1}.[13] The most endothermic chain propagation stages are as follows:[14]

$$\sim CHCl{-}\dot{C}H{-}CHCl\sim \rightarrow \sim CHCl - CH{=}CH\sim + Cl^{\cdot}; \qquad (2)$$

$$\sim CH_2{-}\dot{C}Cl{-}CH_2\sim \rightarrow \sim CH{=}CCl{-}CH_2\sim + H^{\cdot}. \qquad (3)$$

Stage (2) is 83.7 kJ mol^{-1} endothermic and stage (3) is 163.3 kJ mol^{-1} endothermic.[14] After adding together $1/2E_i$ and E_p, neglecting E_t, we obtain E_{eff} = 326.6 kJ mol^{-1} for compounds of the type $\sim(CH_2 - CHCl)_n\sim$ and E_{eff} = 280.5–283.9 kJ mol^{-1} for $\sim(CH{=}CH)_m{-}CHCl\sim$.

For the thermal decomposition of chlorohydrocarbons in the liquid phase in the presence of active chain transfer agents (for example, of thiols) the most endothermic stages (2) and (3) do not occur because the free radicals react with the thiol and the effective activation energy for the thermal decomposition of hydrocarbons becomes equal to approximately half the C–Cl bond energy. Consequently, owing to the decrease of E_{eff} in the presence of active chain transfer agents, there is an increased probability of the decomposition of the chlorohydrocarbons via a radical chain mechanism.

The difference between monochlorohydrocarbons and polychlorohydrocarbons consists in the fact that the thermal decomposition of the latter involves the formation of the polyenes $\sim(CH{=}CH)_m{-}CHCl\sim$, in which the C–Cl bond energy is lower by ~83.7 kJ mol^{-1} than the energy of the same bond in monochlorohydrocarbons. Consequently, they are also characterised by a lower value of E_{eff} for thermal decomposition via a radical chain mechanism.

Thus the radical mechanism for the thermal decomposition of polychlorohydrocarbons which model the fragments of PVC macromolecules can compete with the ionic-molecular mechanism only in the presence of electron donors and active chain transfer agents. In the absence of such additives, the ionic-molecular mechanism predominates.

III. KINETICS OF THE THERMAL DECOMPOSITION OF POLY(VINYL CHLORIDE)

The thermal decomposition of PVC in the presence of HCl is an autocatalytic process.[15–26] Conditions under which critical phenomena are observed have been formulated and equations for the kinetics of the thermal decomposition of the polymer in a closed volume with removal of HCl have been derived.[15,22] The critical size of the polymer specimen, i.e. the maximum thickness of the film for which autocatalysis does not yet develop, is very small:[22] 0.24 mm at 463 K, 0.18 mm at 473 K, and 0.15 mm at 483 K. Hence it follows that correct data for the kinetics of the thermal decomposition of PVC, uncomplicated by autocatalysis, can be obtained only by employing a polymer in the form of a thin layer of powder or a film in a high vacuum. In addition, autocatalysis can be excluded by decomposing PVC in solution, but the solvent must not then exert a significant influence on the dehydrochlorination process.[24]

Fig. 1 presents experimental data for the thermal decomposition of PVC in the form of a thin layer of powder under high vacuum[27] and Fig. 2 illustrates the kinetic curves for the dehydrochlorination of the polymer in solution in 1,2,4-trichlorobenzene.[24] The dehydrochlorination process consists of two stages: initially the rate of reaction falls and after a certain time becomes virtually constant. This shows that unstable fragments of the macromolecules are decomposed initially and, after the complete decomposition, the rate of dehydrochlorination is determined by the decomposition of only the normal units of the PVC macromolecules. An increase in the initial concentration of the unstable fragments leads to an increased initial rate of dehydrochlorination of PVC and hardly affects the steady-rate of the process (Fig. 2).[24]

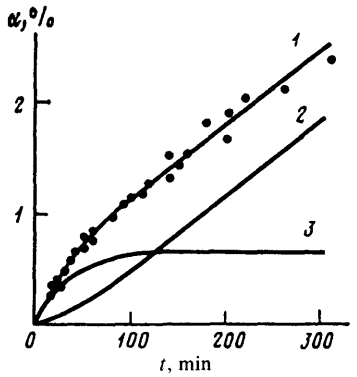


Figure 1. Kinetic curves for the dehydrochlorination of PVC *in vacuo* (~10–2 Pa) at 473 K and with constant freezing out of HCl: 1) experiment; 2) calculation by Eqn. (19); 3) result of the graphical subtraction of curve *2* from curve *1*;[27] α = degree of conversion.

Effective rate constants have been determined for the thermal decomposition of the unstable chloroallyl (k^1_{eff}) and ketochloroallyl ($k_п$) fragments:

$$k^1_{eff} = 10^{9.6\pm0.5} \times e^{-28000\pm1000/RT}\ s^{-1}\ (\text{Refs. 17, 27}),$$
$$k_п = 10^{14.9\pm0.8} \times e^{-36100\pm1700/RT}\ s^{-1}\ (\text{Ref. 26}),$$

as well as normal PVC units:

$$k^0_{eff} = 10^{11.8\pm0.5} \times e^{-38000\pm1000/RT}\ s^{-1}\ (\text{Refs. 17, 27}),$$
$$k_0 = 10^{9.4\pm0.7} \times e^{-21500\pm1500/RT}\ s^{-1}\ (\text{Ref. 26}),$$

where k_0 is the rate constant for the thermal decomposition of the normal units and k^0_{eff} the effective rate constant for their decomposition.

An important characteristic of the thermal decomposition of PVC is the length of the kinetic chain. The average length of the kinetic chain l_{av} can be determined from experimental data on the thermal decomposition of PVC containing unstable fragments at a known concentration by a simple division of the total amount of HCl evolved in the decomposition of all the unstable fragments by their initial concentration. It follows from the literature[24,28] that l_{av} = 4–10. This value of l_{av} is greater than the average number of conjugated double bonds in the polyenes formed, which is 3–5 according to ultraviolet spectroscopic determinations.[24,29] This is associated with the participation of the polyenes in the secondary intra- and inter-molecular cyclisation reactions,[11,20,24,29] which decreases the average number of conjugated double bonds.

The thermal decomposition of "ideal" PVC which contains no unstable fragments can be represented by the following equations[17,25,27]

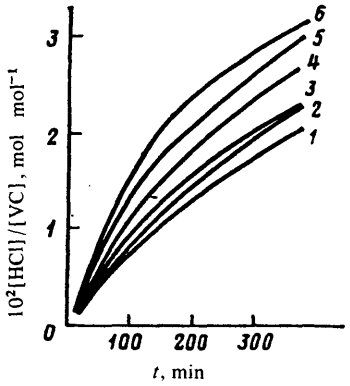


Figure 2. Kinetic curves for the thermal decomposition of PVC (1% solution in 1,2,4-trichlorobenzene) at 473 K for different initial contents of chloroallyl groups (mole %): 1) 0.006; 2) 0.012; 3) 0.017; 4) 0.036; 5) 0.069; 6) 0.107;[24] VC = vinyl chloride.

Initiation:

$$\sim(CH_2{-}CHCl)_n{\sim} \xrightarrow{k_0} HCl + \sim(CH_2{-}CHCl)_{n-1}{-}(CH{=}CH){\sim}. \quad (4)$$

Chain propagation:

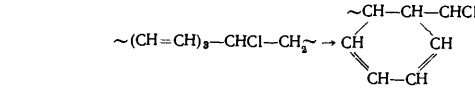
$$\sim(CH_2{-}CHCl)_{n-1}{-}(CH{=}CH){\sim} \xrightarrow{k_1} HCl + \sim(CH_2{-}CHCl)_{n-2}{-}(CH{=}CH)_2{\sim}; \quad (5)$$

$$\sim(CH_2{-}CHCl)_{n-2}{-}(CH{=}CH)_2{\sim} \xrightarrow{k_2} HCl + \sim(CH_2{-}CHCl)_{n-3}{-}(CH{=}CH)_3{\sim}; \quad (6)$$

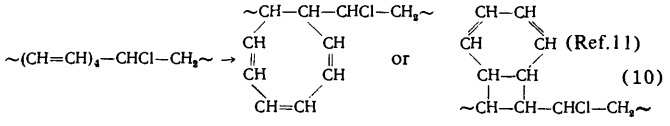
$$\sim(CH_2{-}CHCl)_{n-3}{-}(CH{=}CH)_3{\sim} \xrightarrow{k_3} HCl + \sim(CH_2{-}CHCl)_{n-4}{-}(CH{=}CH)_4{\sim}; \quad (7)$$

$$\sim(CH_2{-}CHCl){-}(CH{=}CH)_{n-1}{\sim} \xrightarrow{k_{n-1}} HCl + \sim(CH{=}CH)_n{\sim}. \quad (8)$$

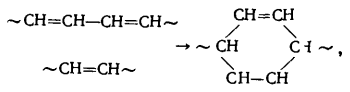
Chain termination:



; (9)



(10)

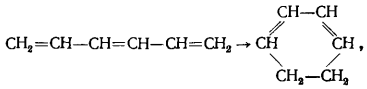


(11)

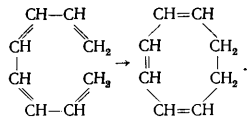
where $n = l_{av}$.

Reaction (4) represents the statistical initiation of the elimination of HCl from any unit of the macromolecules.

The occurrence of the termination reactions (9) and (10) has been confirmed by experiments with low-molecular-weight model compounds. The occurrence of the following cyclisation reactions of trienes and tetraenes has been demonstrated:[30,31]



(12)



(13)

Reactions (12) and (13) are described by first-order kinetic equations with the Arrhenius parameters $\lg A = 11.0$ and $E = 125$ kJ mol^{-1} for reaction (12)[30] and $\lg A = 11.0$ and $E = 71$ kJ mol^{-1} for reaction (13).[31]

The intermolecular polyene cyclisation reaction (11) leads to the formation of a cross-linked polymer.[19]

On the basis of the scheme presented above, the rate of evolution of HCl can be expressed by the equation[17,27]

$$\frac{d[HCl]}{dt} = k_0c_0 + k_1c_1 + k_2c_2 + \ldots + k_nc_n, \quad (14)$$

where k_0, k_1, ..., k_n are the rate constants for different stages, c_0, c_1, c_2, ..., c_n are the concentrations of the corresponding fragments, and $n = l_{av}$.

Using the theory of consecutive reactions,[32] we shall express c_0, c_1, c_2, ..., c_n at time t in terms of c_0^0 (the initial concentration of the ~CH_2–CHCl~ fragments in the polymer) and the rate constants k_0, k_1, ..., k_n:

$$c_0 = c_0^0 e^{-k_0t}, \quad (15)$$

$$c_1 = c_0^0\left[\frac{k_0}{k_1 - k_0}e^{-k_0t} + \frac{k_0}{k_0 - k_1}e^{-k_1t}\right], \quad (16)$$

$$c_2 = c_0^0\left[\frac{k_0k_1}{(k_1 - k_0)(k_2 - k_0)}e^{-k_0t} + \frac{k_0k_1}{(k_0 - k_1)(k_2 - k_1)}e^{-k_1t} + \right.$$
$$\left. + \frac{k_0k_1}{(k_0 - k_2)(k_1 - k_2)}e^{-k_2t}\right] \text{ etc.} \quad (17)$$

Having substituted the value of c_0, c_1, c_2, etc. [Eqns. (15)–(17)] in Eqn.(14), subject to the condition $k_0 \ll k_1 \ll k_2 \cong k_n$ (this has been demonstrated for model compounds[2–10]), we arrive at a greatly simplified formula:[17,27]

$$\frac{d[HCl]}{dt} = k_0c_0^0 l_{av}\left(e^{-k_0t} - \frac{l_{av} - 1}{l_{av}}e^{-k_1t}\right). \quad (18)$$

Integration of Eqn.(18) yields an expression for the concentration of HCl:

$$[HCl] = l_{av}c_0^0(1 - e^{-k_0t}) - (l_{av} - 1)c_0^0\frac{k_0}{k_1}(1 - e^{-k_1t}). \quad (19)$$

It can be shown that $k_{eff}^0 = k_0l_{av}$ and $k_{eff}^1 = k_1l_{av}$.[17,27] Knowing k_{eff}^0, k_{eff}^1, and l_{av}, it is possible to determine k_0 and k_1. The constants k_0, k_1, and l_{av} obtained by different workers[17,24,27,33,34] are listed in Table 2.

Comparison of Tables 1 and 2 shows that the rate constants for the decomposition of fragments of the PVC macromolecules are close to the rate constants for the thermal decomposition of the model compounds in the liquid phase.

Having substituted the values of k_0, k_1, and l_{av}[17,27] in Eqn.(19), it is possible to calculate the time variation of the HCl concentration in the decomposition of the "ideal" polymer which does not contain unstable fragments (Fig.1, curve *2*). The existence of a certain initial section of curve *2* where the rate of formation of HCl increases is striking. After that, the rate no longer changes. The increase in the rate of formation of HCl is associated with the accumulation and decomposition of fragments containing carbon–carbon double bonds: initially the rate of accumulation of such fragments is greater than the rate of decomposition but afterwards the two rates approach one another and equilibrium is attained at a constant concentration of the chloroallyl fragments. The equilibration time depends on the rate constant ratio k_0/k_1, which follows from Eqn.(19).

Table 2. Arrhenius parameters for the thermal decomposition reactions of fragments of PVC macromolecules.

Polymer fragment	$\lg A$, s^{-1}	E, kJ mol^{-1}	Phase	ΔT, K	l_{av}	Refs.
~CH_2–CHCl~	11.0	159	polymer melt	453—523	8	[17, 27]
~CH=CH–CHCl–CH_2~	9.8	113	ditto	453—483	8	[17, 27]
~CH_2–CHCl~	3.4	90	»	418—448	—	[34]
~CH=CH–CHCl–CH_2~	—	—	»	453	8	[33]
~CH=CH–CHCl–CH_2~	—	—	polymer solution	473	10—13	[24]

Fig.1 demonstrates the discrepancy between the experimental curve *1* and the theoretical curve *2* calculated by Eqn.(19). This means that the initial rate of thermal decomposition of PVC is determined not only by the statistical decomposition of the normal units of the macromolecule but also by the thermal decomposition of unstable fragments always present in the initial polymer. Graphical subtraction of curve *2* from curve *1* yields the kinetic curve for the thermal decomposition of the unstable fragments alone (curve *3*).

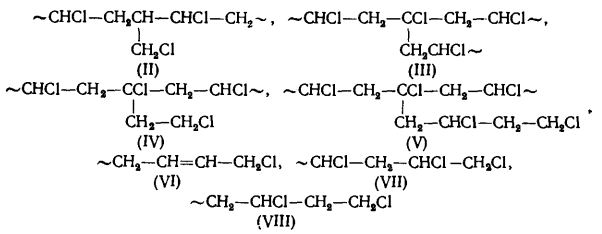
Fig.1 clearly illustrates the contribution of two thermal decomposition processes, initiated by the statistical decomposition of the normal units (curve *2*) and the unstable fragments (curve *3*), to the overall dehydrochlorination reaction of real PVC as a function of time. Knowing l_{av} and the amount of HCl evolved in the decomposition of all the unstable fragments (which can be readily determined from curve *3* in Fig.1), it is possible to estimate the concentration of the unstable fragments in PVC. For the PVC specimen whose thermal decomposition is illustrated in Fig.1, it amounts to ~0.08 mole %.

IV. THE NATURE OF THE UNSTABLE FRAGMENTS IN POLY(VINYL CHLORIDE) MACROMOLECULES

The controversy concerning the nature and concentration of the unstable fragments in PVC macromolecules and also the contribution of each of them to the initial rate of thermal decomposition of the polymer has continued for a long time.[7,9–11,15,24,28,29,33–50] The difficulty of the solution of this problem consists in the fact that the unstable fragments are present in the polymer at low concentrations.

The concentration of double bonds in PVC has been determined by the bromination[36,44] and ozonolysis[24,33,34,40] methods as 0.1–0.5 mol %. By combining the ozonolysis method with hydrolysis and subsequent determination of the molecular weight distribution (MWD) of the polymer[24,33,40] by ^{13}C NMR[44,47] and other procedures,[39] it was established that PVC contains 0.01–0.05 mole % of internal chloroallyl fragments. The bulk of the double bonds in PVC are located either at the ends or near the ends of the macrochains.

The question of the presence of a chlorine atom at a tertiary carbon atom in PVC has been the subject of controversy for many years. A convenient method has been developed[11,35] for the reduction of PVC to polyethylene using Bu_3SnH or Bu_3SnD as the reducing agent. Analysis of the ^{13}C NMR spectra of the reduced PVC demonstrated the presence of the following fragments in the polymer:[11,35,43,44]



The contents of the fragments (II)–(V) in different PVC specimens are presented in Table 3.

Table 3. Concentrations of branched structures in PVC macromolecules.[35]

Brand of PVC	T_p, K*	No. of fragments per 1000 monomer units			
		(II)	(III)	(IV)	(V)
A	373	4.0	0.6	1.6	1.8
B	373	4.4	0.8	1.4	1.6
S-54	348	5.6	0.6	1.2	2.0
E-54	348	4.4	0.6	0.6	1.0
P-23	329	4.2	0.4	0.2	0.4
S-80	316	4.4	0.4	0.6	1.4
E-80	316	4.0	0.6	1.0	1.2
103EP	—	5.2	0 4	0.6	1.2

*T_p = polymerisation temperature of vinyl chloride.

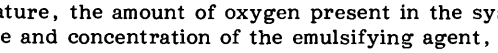
For different brands of PVC, obtained at temperatures ≤348 K, the overall concentration of the fragments containing a chlorine atom at a tertiary carbon atom is 0.1–0.28 mole %.[11,35,43,44]

PVC contains smaller amounts (0.01 mole %) of peroxy- and hydroperoxy-groups[33,36–38] and up to 0.02 mole % of internal fragments with a "head-to-head" structure.[48]

It has been demonstrated on model compounds that the peroxy- and hydroperoxy-groups as well as units of the polymer chain containing a chlorine atom in the allyl position (~CH=CH–CHCl–CH_2~) or at a tertiary carbon atom are unstable fragments of PVC macromolecules which readily decompose,[22–10,46] A group of investigators have carried out special experiments designed to synthesise PVC specimens containing low concentrations of the above unstable fragments.[24,28,33,45] It has been shown that an increase in the concentration of the internal chloroallyl fragments,[24,33,39,40,45] groups with chlorine atoms at a tertiary carbon atom,[28,43,44] and peroxy- and hydroperoxy-fragments[33,37,38] in the polymer appreciably increases the initial rate of thermal decomposition of the polymer.

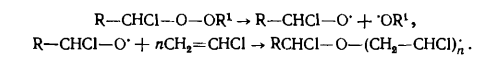
The formation of all the unstable fragments in the initial PVC is determined by the characteristic features of the radical polymerisation of vinyl chloride and their quantitative content is directly related to the technological parameters of a specific process: the purity of the monomer, the concentration and nature of the initiator, the polymerisation temperature, the amount of oxygen present in the system, the type and concentration of the emulsifying agent, the suspension stabiliser and other additives, the degree of completion of the polymerisation process, the degree of purification of the water used, etc.

The presence of oxygen in the polymerisation of vinyl chloride leads to the formation of polymeric peroxides and hydroperoxides.[33,38,51] Their decomposition via the general mechanism[33,38,51]



takes place simultaneously with the formation reaction. After polymerisation, up to 20–30% peroxy- and hydroperoxy-groups remain undecomposed in the polymer.[38]

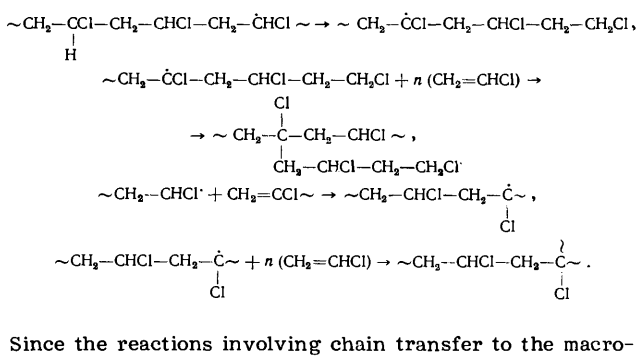
In the decomposition of polymeric peroxides in the presence of an excess of the monomer, i.e. under the conditions of the polymerisation of vinyl chloride, there is a possibility that fragments of the polymeric peroxides are incorporated as end groups in the PVC macromolecule:



Judging from the parameters of the thermal decomposition of model compounds containing an alkoxy-group in the α-position relative to the C–Cl bond, the RCHCl–OR^1 fragments can also be classified as unstable groups in PVC macromolecules (Table 1).

It has been established[50] that the polymer formed on polymerisation of vinyl chloride under the conditions of a reduced pressure of the monomer contains a greater amount of unstable fragments, in particular branched structures with a chlorine atom at a tertiary carbon atom, and its thermal stability is lower.

The following mechanisms have been proposed for the formation reactions of the branched fragments with mobile chlorine atoms:[11,35]



Since the reactions involving chain transfer to the macromolecule in the polymerisation of vinyl chloride compete with the chain propagation reactions, whose rate is determined by the concentrations of the macroradicals and the monomer, it follows that the rate of the interaction of the macroradicals with the polymer molecule and the probability of the formation of unstable fragments increase with decrease in the monomer concentration.

Thus it has now been established that, in the usual brands of PVC, the highest concentration of unstable fragments is that of chlorine atoms at the branching sites (0.1–0.28 mole %). Consequently they should in fact exert a decisive influence on the initial rate of thermal decomposition of the polymer.[11,35,43,44] The quantitative contribution of other unstable groups (peroxy-, hydroperoxy-, and chloroallyl) and possibly also fragments of the type ~CH_2–CCl(OR)~ and ~O–CH=CH–CHCl~ to the initial rate of thermal decomposition of the polymer remains obscure. The influence of conditions in the polymerisation of vinyl chloride on the quantitative content of each unstable fragment in the polymer has not been adequately investigated.

The role of the ~C(O)–CH=CH–CHCl~ fragments in the thermal decomposition of PVC is not considered in this review, since this question has been discussed exhaustively in a recently published book[42] and review.[34]

V. THE MECHANISM OF THE THERMAL DECOMPOSITION OF POLY(VINYL CHLORIDE) IN THE ABSENCE OF HCl

There exist two theories of the thermal decomposition of PVC: the ionic-molecular[11,17,24,33,41] and radical[37,52,53] theories. According to the radical theory, the principal active species involved in the chain propagation reactions is atomic chlorine. Metals behave as effective acceptors of atomic chlorine. Mercury and silver (metals which do not interact with HCl) do not affect the rate of dehydrochlorination of PVC *in vacuo* after being added to the polymer even in large amounts (in 1 : 1 proportions by weight).[16] Mercury vapour does not retard the thermal decomposition of PVC in the absence of HCl either.[52] These findings show that the thermal decomposition of PVC proceeds mainly via an ionic-molecular mechanism. Data for the thermal decomposition of model compounds in the liquid phase (Section II) also serve as an argument in support of the ionic-molecular mechanism.

The occurrence of radical processes in the thermal decomposition of the polymer is indicated by the following experimental data. Apart from HCl, benzene is evolved in small amounts in the reaction (a factor of 100–1000 less then HCl), its yield diminishing in the presence of free radical inhibitors such as nitric oxide and α-naphthol.[22,52] The peroxides and hydroperoxides present at low concentrations in the polymer increase the initial rate of thermal decomposition of PVC.[33,37,53] However, it has been shown by the inhibitor method that the formation of HCl via the radical mechanism is a process involving very short chains (the chain length is ~2).[52] It follows from the experimental data for the thermal decomposition of PVC containing a specified amount of polymeric peroxides[33] that the average chain length of the radical dehydrochlorination reaction is ~2. This agrees with the above results.[52] The short chain length (~2) is apparently associated with the endothermic nature of the chain propagation stages (2) and (3), which hinders the radical chain process.

Thus the thermal decomposition of PVC in the absence of HCl proceeds mainly via the ionic-molecular mechanism complicated by radical reactions.

VI. THE MECHANISM OF THE AUTOCATALYTIC DECOMPOSITION OF THE POLYMER

The autocatalysis of the thermal decomposition of PVC is explained by the interaction of HCl with polyenes.[16,18,21,54] Definite information about the mechanism of this process is provided by experiments on its retardation by compounds which do not interact with HCl.[16,17,19–21,55–61] The stabilising effect of these compounds cannot be explained by the destruction of the catalyst.

Catalysis is not observed in the thermal decomposition of PVC powder in sealed evacuated bulbs in the presence of maleic anhydride, although HCl does accumulate in the bulbs.[21,55] The autocatalytic decomposition of PVC is suppressed by mercury, silver (in the form of a finely dispersed powder mixed with the polymer particles),[16,52,57] trialkylsilanes,[58,59] and the chlorides of coordination-unsaturated metals at microconcentrations.[17,56,60,61]

We shall now discuss the experimental data obtained from the standpoint of the radical and ionic theories of the autocatalytic decomposition of PVC. As shown in Section II, in the presence of active chain transfer agents, the probability of the radical thermal decomposition reactions of polychlorohydrocarbons should increase as a consequence of the suppression of the most endothermic chain propagation stages (2) and (3). Hydrogen chloride is a low-molecular-weight compound which readily diffuses in PVC and can play the role of a chain transfer agent and hence increase the rate of the radical chain thermal decomposition reaction of the polymer.

Mercury and silver can accept chlorine atoms; they should inhibit the radical thermal decomposition of PVC. However, from the standpoint of the radical chain dehydrochlorination of PVC in the presence of HCl, it is difficult to account for the suppression of the autocatalytic dehydrochlorination of PVC by maleic anhydride and metal chlorides at microconcentrations and also the fact that the usual inhibitors of free-radical reactions, namely toluene, diphenylmethane, and sterically hindered phenols, do not have an appreciable retarding effect on the autocatalytic decomposition of the polymer.[20,21,52,62] Maleic anhydride enters into the Diels–Alder reaction, but only with dienes having the cisoid structure. However, polyenes with the transoid configuration remain in the polymer and the radical chain process should therefore have developed. The chlorides of coordination-unsaturated metals react with polyenes to form paramagnetic charge-transfer complexes[63] whose involvement in the inhibition of radical reactions is difficult to explain.

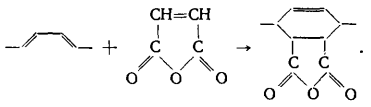
The radical chain theory of the autocatalytic decomposition of PVC also fails to explain the absence of a catalytic influence of HCl on the thermal decomposition of poly(vinylidene chloride) (PVDC),[17,20,23,64,65] a polymer whose chemical structure is close to that of PVC, and the accelerating effect of Cl_2 and Br_2 on the thermal decomposition of PVC, while no such effect is observed in the thermal decomposition of PVDC.[64]

The available experimental data can be accounted for by assuming that the interaction of HCl with polyenes results in the formation of charge-transfer complexes (CTC) in which the polyene behaves as the donor and HCl as the acceptor, the HCl reacting predominantly with polyenes having the cisoid structure:[17,27]

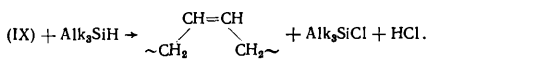
$[ClHCl]^{\ominus}$
(IX)

The complex $H^{\oplus}[ClHCl]^{\ominus}$ is a stronger electron acceptor than HCl, since the energy gain on formation of $[ClHCl]^-$ is 79.2 kJ mol^{-1}.[66] The ion pairs (IX) initiate the thermal decomposition of PVC via a heterolytic mechanism.

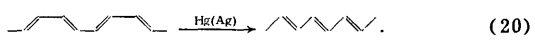
The inhibiting effect of maleic anhydride on the autocatalytic decomposition of PVC can be explained by the Diels–Alder reaction with *cis*-polyenes:



Trialkylsilanes reduce compound (IX) via the reaction[17]



The mercury and silver atoms interacting with polyenes can play the role of catalysts of the *cis–trans* isomerisation of the latter:



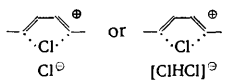
(20)

trans-Polyenes are thermodynamically more stable at 440–480 K than the *cis*-polyenes, since it is known[67] that, on heating above 373 K, *cis*-polyacetylene is converted into *trans*-polyacetylene.

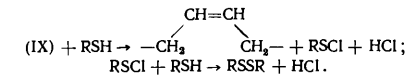
The paramagnetic CTC of the chlorides of coordination-unsaturated metals with polyenes can also play the role of catalysts of reaction (20).

The thermal decomposition of PVDC leads to the formation of polyenes with bulky electron-accepting substituents (chlorine atoms), which hinders their interaction not only with HCl but also with Cl_2 and Br_2. For this reason, these additives do not show an accelerating effect.[64]

The catalytic effect of Cl_2 and Br_2 on the thermal decomposition of PVC[64] can also be accounted for by the formation of an active intermediate species (ion pair) on interaction of the *cis*-polyene with the additive:



It may be that the reaction (1) of thiols with chlorohydrocarbons[11] also proceeds via the mechanism



In contrast to monochlorohydrocarbons, polychlorohydrocarbons give rise to polyenes on thermal decomposition, which interact with the acceptor (HCl) more readily than compounds with a single double bond.

Some workers believe that the autocatalysis is associated with the influence of HCl on the decomposition of the normal PVC units.[15,22,52]

Experimental data obtained recently lead to the conclusion that the autocatalytic decomposition of PVC in the presence of HCl has an ionic mechanism.[15,17,52,54]

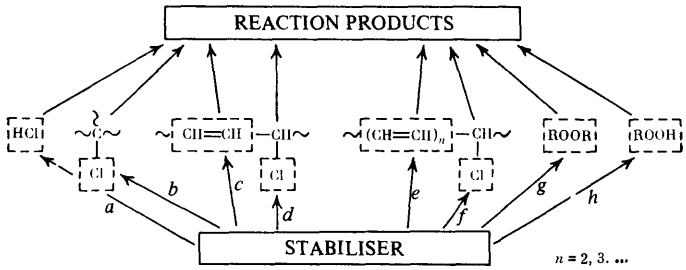
VII. THE MECHANISM OF THE ACTION OF EFFECTIVE STABILISERS OF POLY(VINYL CHLORIDE) IN ITS THERMAL DECOMPOSITION

The following procedures for reducing the rate of the autocatalytic decomposition of PVC follow from the ideas concerning the influence of HCl on the decomposition of the polymer: (1) by binding the HCl; (2) by interaction of the stabiliser with the double bonds (conjugated double bonds), and (3) by inhibition of the heterolytic chain reaction as a result of the deactivation of the ion pairs.

The initial rate of the non-catalytic decomposition can be reduced by reducing the concentration of the unstable fragments and the chain length l_{av} in the consecutive dehydrochlorination reaction.

It follows from Scheme 1 that the stabilisation of PVC is based on reactions of the stabiliser with HCl (*a*), reactions involving the nucleophilic substitution of the labile chlorine atoms by groups which are more strongly bound to the polymer (*b*, *d*, and *f*), reactions involving the addition to double (*c*) and conjugated double (*e*) bonds, and the decomposition of peroxides and hydroperoxides (*g* and *h*).

Scheme 1



The classification of stabilisers of PVC can be based on different features. It has been suggested that stabilisers be divided into two groups: (1) stabilisers acting on the non-catalytic HCl formation reaction and (2) stabilisers preventing the catalytic dehydrochlorination.[52] A method has been developed for determining the critical concentration of the HCl acceptors.[52,68] The classification based on the chemical structures of the stabilisers has been most widely adopted.

A classification of the PVC thermostabilisers based on their reactivities towards the units of the macrochains has also been proposed.[17]

The first group includes Group IA and IIA metal carboxylates,[20,68–70] compounds of the type R_4Sn (R = alkyl or aryl) and Ph_4Pb,[20] organic phosphites,[20,69,71,72] epoxy-compounds,[42,69] maleic anhydride (acid), maleate esters,[20,21,55,69,73,74] organosilicon and organogermanium hydrides,[58,59] oligosilanes,[75] and other compounds.[69] It has been shown[17,20,21,55,58,59,71,75] that the main stabilising function of the above compounds consists merely in reducing the rate of the autocatalytic decomposition of the polymer. The rate of the thermal decomposition of PVC in the presence of such stabilisers at best approaches the rate of its non-catalytic dehydrochlorination. These stabilisers are relatively inactive in nucleophilic substitution reactions (Scheme 1, reactions *b*, *d*, and *f*).

The second group includes the most effective PVC thermostabilisers: organotin derivatives of maleic and thioglycolic acids having the structures R_2SnX_2, $R_2Sn(OOCCH{=}CHCOO)$, and R_3SnX, where R = alkyl, X = OOCCH=CHCOOR, or SCH_2COOR,[20,69,76–83] as well as multicomponent synergistic mixtures based on Ca–Zn and Ba–Cd carboxylates.

Organic acid (except for maleic and thioglycolic acids) salts of dialkyltin, trialkyltin carboxylates,[20,69,83] triaryltin isocyanates,[84] cadmium carboxylates,[20,69,70,85] binary synergistic mixtures including zinc, cadmium, or dialkyltin carboxylates as well as an organic phosphite,[20,69,71,72] an organotin compound and an organic phosphite,[20,86] an organolead compound and an organic phosphite,[87] an organic phosphite and the chloride of a coordination-unsaturated metal,[20,71] an organosilicon or an organogermanium hydride and the chloride of a coordination-unsaturated metal,[88] the carboxylate of a coordination-unsaturated metal and a compound with OH, SH, and NH groups,[89–95] as well as ternary synergistic mixtures consisting of Ca–Zn carboxylates and a polyol, Ba–Cd

carboxylates and a polyol,[89,91,93-96] Group II metal carboxylates and epoxy-compounds,[42,69,97,98] and others[42,69] approach the second group in terms of the efficiency of their action.

In the presence of the above stabilisers the rate of dehydrochlorination of the polymer is several times lower [in the best case, in the presence of bis(alkyl maleate)dialkyltin derivatives, by a factor of 8[76]] than the rate of the non-autocatalytic decomposition of PVC. The efficiency of the action of the stabiliser is characterised by a period T from the start of decomposition in the presence of the stabiliser to the sharp increase in the rate of dehydrochlorination of PVC. In the thermal decomposition of PVC in the presence of stabilisers belonging to the second group, no colour change is observed during the period T and a cross-linked polymer is not formed. The stabilisers of this group participate in all the reactions indicated in Scheme 1.

The third group includes zinc carboxylates,[69,89-96] triphenyl-lead isocyanate,[87] organotin compounds having the structures $Ph_2Sn(OOCCH{=}CHCOO)$, Ph_2SnX_2, $RSnX_3$, and $R_2Sn(SCH_2COO)$, where R = alkyl and X = OOCCH=CHCOOR or SCH_2COOR,[69,76,83] and other compounds. They too are effective PVC stabilisers, but, in terms of the period T, they are appreciably inferior to compounds of the second group. Their characteristic feature is the formation, in the interaction with HCl and with fragments of the macrochains, of metal chlorides which are powerful catalysts of the dehydrochlorination of the polymer and of the reaction of the stabiliser with the normal units. This leads to the rapid consumption of the stabiliser and hence to the shortening of the period T.

In recent years much attention has been devoted to the study of the mechanism of the action of organotin compounds[11,17,34,42,69,76-83] and synergistic mixtures,[11,17,42,69,86-99] which effectively stabilise polymers and are widely used in practice.

1. Organotin Compounds

(a) Kinetics of the Thermal Decomposition of PVC in the Presence of Organotin Derivatives of Maleic and Thioglycolic Acids

We shall consider the kinetics of the thermal decomposition of PVC in the presence of the most effective stabilisers—organotin derivatives of maleic and thioglycolic acids. As an example, Fig. 3 presents the kinetic curve (curve *3*) for the accumulation of ionic chlorine in the thermal decomposition of the polymer in the presence of $Bu_2Sn(OOCCH{=}CHCOOC_6H_{11})_2$. Three sections can be distinguished in the curve: along the first section, the rate continually diminshes, along the second it is constant, and along the third it rises sharply.

The initial section of the kinetic curve corresponds to the interaction of the unstable fragments with the stabiliser. The presence of the stationary section shows that all the unstable units of the initial polymer have reacted with the stabiliser and a constant rate of thermal decomposition, initiated by the statistical disruption of the normal units of the macrochain, is established. The acceleration of the dehydrochlorination of PVC along the third section of curve *3* (Fig. 3) is caused by the development of the catalytic decomposition of PVC.

It has been demonstrated by γ-resonance spectroscopy [Mössbauer spectroscopy][79] that the organotin derivatives of maleic and thioglycolic acids Oct_2SnX_2, where X = OOCCH=CHCOOOct-iso or $SCH_2COOOct$-iso and Oct = octyl, mixed with PVC are converted into $Oct_2SnCl(X)$ at the end of the period T at 458 K and not into Oct_2SnCl_2, as suggested earlier by many investigators.

It is also seen from the kinetic data (Fig. 3, curve 3)[76] that at the end of the period T one acid residue in $Bu_2Sn(OOCCH{=}CHCOOC_6H_{11})_2$ is substituted by chlorine. During the first 70 min, 85% of dibutylbis(cyclohexyl maleate)tin is consumed and only 15% in the next 200 min (up to the end of the period T), i.e. almost the entire stabiliser is consumed in reactions with the active fragments present in the initial polymer.

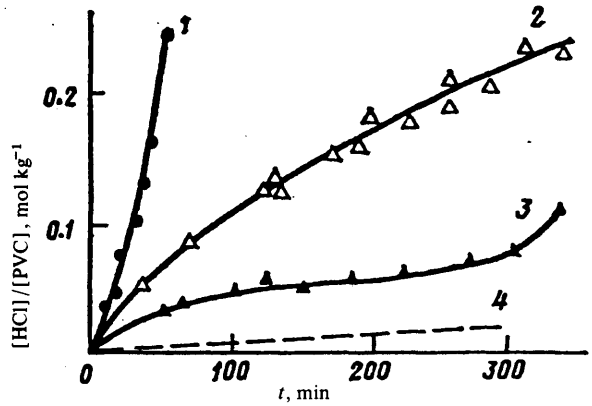


Figure 3. Kinetic curves for the dehydrochlorination of PVC at 463 K: 1) in evacuated (up to ~10^{-2} Pa) sealed tubes without the removal of volatile products; 2) *in vacuo* (~10^{-2} Pa) with constant removal of volatile products; 3) formation of ionic chlorine in the decomposition of PVC in evacuated sealed tubes containing added dibutylbis(cyclohexyl maleate)tin at a concentration of 7.0×10^{-2} mol/kg PVC; 4) theoretical curve for the dehydrochlorination of PVC in the presence of the "ideal" stabiliser.[17,76]

When the stationary section of curve *3* (Fig. 3) is extrapolated to the ordinate axis, an intercept is obtained, corresponding to the concentration of the stabiliser which has reacted with the active fragments and hence also to the concentration of the active fragments in the given PVC specimens (~2 per 1000 monomeric units).

The steady-state rate of thermal decomposition of the polymer in the presence of the stabiliser makes it possible to calculate l_{av} for the thermal decomposition of PVC *in vacuo*.[17,76] It has been established[100,101] that dialkyltin carboxylates readily undergo the exchange reaction with the chloroallyl fragments of PVC, substituting the labile chlorine atoms by groups which are more strongly bound to the polymer chains. It has been shown[11] that, after heating PVC with $Bu_2Sn(SC_{12}H_{25})_2$ or with a mixture of this compound and Bu_2SnCl_2 and the subsequent removal of the stabiliser from the polymer, the rate of thermal decomposition of PVC diminishes in proportion to the number of stabiliser fragments introduced into the PVC, which confirms the proposed[100] mechanism of the stabilisation of the polymer by organotin compounds.

Bis(alkyl maleate)dialkyltin derivatives react only slightly with the normal PVC units[76,102] and the slope of the steady-state section of curve *3* (Fig. 3) therefore corresponds to the rate of formation of dialkyltin chlorides when the stabiliser reacts with HCl and with the chloroallyl fragments arising on

decomposition of the normal units of the macrochains. Ultraviolet spectra show[17,76] that there is virtually no absorption at $\lambda > 280$ nm in the thermal decomposition of PVC in the presence of the given stabilisers, i.e. polyenes are virtually not formed and the average dehydrochlorination chain length is $l_{av}^{st} \cong 1$. Having divided the rate of formation of ionic chlorine along the steady-state section by two, it is possible to obtain the rate of dehydrochlorination of the normal PVC units for $l_{av}^{st} = 1$. Division of the steady-state rate of the thermal decomposition of PVC *in vacuo* without the stabiliser (curve *2*, steady-state section) by the rate of its decomposition in the presence of a stabiliser for $l_{av}^{st} = 1$ yields $l_{av}/l_{av}^{st} = 8$, whence $l_{av} = 8$.[17,76]

Fig. 3 also presents the theoretical curve (curve *4*) for the thermal decomposition of PVC in the presence of the "ideal" stabiliser, whereupon the dehydrochlorination of the unstable fragments is fully prevented and the decomposition of the normal unit proceeds with $l_{av}^{st} = 1$. Evidently the organotin derivatives of maleic acid approach the "ideal" polymer thermostabilisers as regards the efficiency of their action.

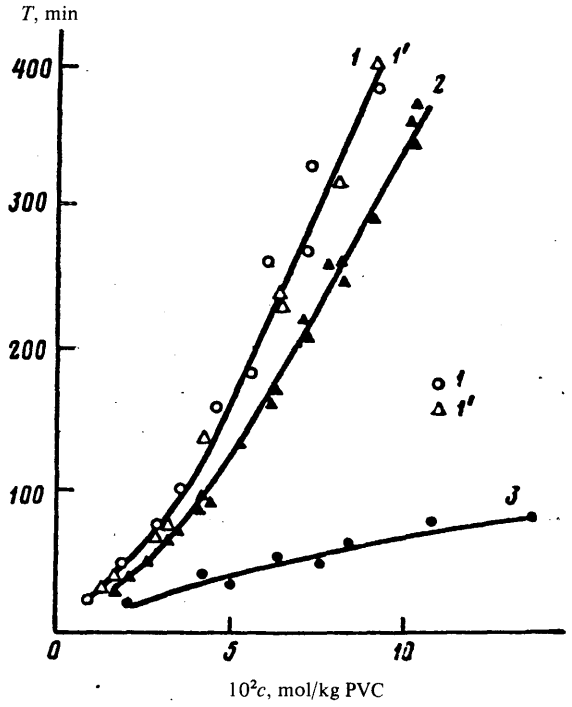


Figure 4. Dependence of the period T on the concentration of organotin maleates (c) in the thermal decomposition of PVC at 463 K: 1) dibutylbis(cyclohexyl maleate)tin; 1') bis(octyl maleate)dioctyltin; 2) dibutyltin maleate; 3) diphenyltin maleate.[76]

(b) Dependence of the Efficiency of the Stabilising Action of Organotin Compounds on Their Chemical Structure

The efficiency of the stabiliser over a wide range of concentrations can be estimated from the curves relating the period T to the concentration of the compound. It is seen from Fig. 4 that stabilisers of the type of bis(alkyl maleate)-dialkyltin derivatives are the most effective. At low stabiliser concentrations there is an inflection in the curve (curves *1* and *2*), after which the efficiency increases. The concentration of the stabiliser corresponding to the point of inflection can be called the second critical concentration. Its significance is that the rate of the bimolecular reaction of the stabiliser with unstable fragments becomes greater than the rate of decomposition of the unstable fragments from this point. The first critical concentration is that at which the rate of dehydrochlorination of the polymer diminishes in the presence of the stabiliser and the period T begins.[52,68,85]

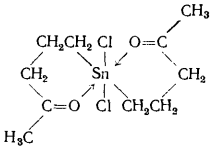
Bis(alkyl thioglycolate)dialkyltin derivatives are close in their efficiency to bis(alkyl maleate)dialkyltin derivatives, but they have one distinguishing feature, which has been noted by Troitskii et al.[76] It has been shown in model reactions[76,102] that compounds with the Sn–S bond are very reactive in nucleophilic substitution reactions with alkyl halides, which shortens the period T. The following series based on the efficiency of the stabilising effect of organotin stabilisers has been obtained from the dependence of the period T on the concentration:[17,76]

$Alk_3SnOOCCH{=}CHCOOSnAlk_3$, $Alk_2Sn(OOCCH{=}CHCOOR)_2 >$
$> Alk_2Sn(OOCCH{=}CHCOO)$, $Alk_2Sn(SCH_2COOR)_2 >$
$> Alk_3SnOOCCH{=}CHCOOR > Alk_3SnSCH_2COOR > Ph_2Sn(SCH_2COOR)_2 >$
$> AlkSn(OOCCH{=}CHCOOR)_3$, $AlkSn(SCH_2COOR)_3 > Alk_2Sn(SCH_2COO) >$
$> Ph_2Sn(OOCCH{=}CHCOO)$, $Ph_2Sn(OOCCH{=}CHCOOR)_2$ where Alk =
$=$Me, Bu, Oct; R=Et, Bu, Oct, C_6H_{11}, $-CH_2-CH_2-$,
$-CH_2-CH_2-OEt$, $-CH_2-CH_2-O-CH_2-CH_2-$.

The efficiency of the last member of the series is ten times smaller than that of the first.

In terms of the rate of interaction with s-BuCl (the low-molecular-weight model of the normal units of the PVC macrochain), organotin compounds can be arranged in a series which is the opposite of that based on the efficiency of the stabilising action.[76]

An increase in the stabilising effect is achieved when the carbonyl group is introduced into the substituent R in compounds of the type $R_2Sn(SCH_2COOR^1)_2$.[78] Thus $[CH_3C(O)CH_2CH_2CH_2]_2Sn(SCH_2COOOct)_2$ is twice as effective as the dibutyltin derivative.[78] The carbonyl group can form intramolecular complexes in dialkyltin dichlorides produced by the interaction of the stabiliser with HCl:



The catalytic activity of Alk_2SnCl_2 in such complexes is reduced.[78]

A sharp impairment of the stabilising activity of the compounds $R_2Sn(SCH_2COOR^1)_2$ is observed for R = CH_2Br or p-$CH_3OC_6H_4$, which is associated with the ease of cleavage of the Sn–C bond under the influence of HCl and the formation of a stronger catalyst of the thermal decomposition of the polymer, namely $SnCl_4$.[78]

Organotin derivatives of thioglycolic acid are more effective PVC thermal stabilisers than the derivatives of thioalcohols.[78] The authors[78] explained this by the fact that thioglycolic acid esters interact more readily with the double bonds than thioalcohols, since they give higher chain transfer rate constants. The introduction of a halogen atom (Cl, Br) into the acid residue of organotin derivatives of maleic acid diminishes the efficiency of their stabilising action.[103]

(c) The Interaction of Organotin Compounds with Low-Molecular-Weight Models of PVC

The reactions of the stabilisers of the type Bu_2SnX_2, where $X = SC_{12}H_{25}$, SCH_3, $O(O)CCH_3$, or $O(O)CC_{11}H_{23}$, with 2-chloro-2-methylbutane, 3-chlorobut-1-ene, and 1-chlorobut-2-ene have been investigated in detail.[77]

The following reactions take place in sealed tubes at 453 K;

$$RCl + Bu_2SnX_2 \rightarrow RX + Bu_2Sn(X)Cl,$$
$$2RCl + Bu_2SnX_2 \rightarrow 2RX + Bu_2SnCl_2,$$

where RCl is a chlorohydrocarbon.

Compounds with the Sn–S bond react more readily with model substances containing double bonds than with substances having a Cl atom at a tertiary carbon atom. The opposite behaviour has been observed for organotin carboxylates.[77]

It has been established[77] that the reaction of Bu_2SnX_2 with model compounds containing a double bond is accompanied by a rearrangement—a shift of the double bond. Bu_2SnCl_2 at low concentrations catalyses the rearrangement.

The interaction of the organotin compounds $RSnX_3$, R_2SnX_2, and R_3SnX, where $X = OOCCH{=}CHCOOR^1$ or SCH_2COOR^1, R = Me, Bu, Oct, or Ph, and R^1 = Et, Bu, Oct, or C_6H_{11}, with s-BuCl, which models the normal units of PVC macromolecules, at 453 K in evacuated sealed tubes has been studied.[76,102] As noted above, in terms of the rate of their interaction with s-BuCl, the compounds investigated can be arranged in a sequence which is the opposite of that based on the stabilising efficiency. In other words, the increased reactivity of the organotin compound leads to its rapid consumption in the nucleophilic substitution reaction with the normal units of the PVC macromolecules, which naturally diminishes the period T.

The reactions of organotin compounds with s-BuCl are accelerated by the products (alkyltin chlorides),[76,102] the catalytic effect diminishing in the following sequence:

$$SnCl_4 > AlkSnCl_3 > Alk_2SnCl_2 > Alk_3SnCl.$$

Thus an effective PVC stabiliser must possess the optimum reactivity towards the chlorine-containing units of the PVC macromolecules: on the one hand, it must interact vigorously with the unstable fragments of the macromolecules, and the rate of such bimolecular reaction must be higher than the rate of unimolecular thermal decomposition of the fragments, while, on the other hand, it should hardly react with the normal PVC units, since this decreases the duration of the stabilising action.

2. Synergistic Mixtures

Synergism is a phenomenon in which the stabilising action of a mixture of two or several substances exceeds the sum of the protective activities of the individual components. This phenomenon is very common in the stabilisation of polymers. The fundamental principles and mechanism of the synergistic action of binary mixtures of stabilisers in the thermo-oxidative and photo-oxidative ageing of polymers have been formulated in a book.[1]

A characteristic feature of PVC which distinguishes it from the majority of other polymers is that synergism is common in the stabilisation with respect to not only its thermo-oxidative or photo-oxidative ageing but also its thermal decomposition in the absence of oxygen. This is associated with the fact that the thermal decomposition of PVC is influenced by HCl and numerous unstable fragments of the macromolecules (Scheme 1) and that one compound cannot as a rule participate effectively in all the reactions simultaneously (certain organotin derivatives of maleic and thioglycolic acids, examined above, are an exception).

The possibilities for the combination of various compounds, each of which participates preferentially in a particular reaction (or group of reactions), are very great and numerous binary, ternary, etc. mixtures of this kind are therefore known.

Some of the products of reactions *a–h* in Scheme 1 (for example the chlorides of coordination-unsaturated metals) are, on the one hand, catalysts of reactions *b–g* (positive effects for stabilisation) and, on the other hand, they catalyse the interaction of the stabiliser with the normal units and accelerate the thermal decomposition of the polymer (negative effect). In order to attain the optimum stabilising effect, the reactivity of metal chlorides is therefore regulated by introducing complex-forming agents, which increases still further the number of synergistic mixtures.

Since reactions *a–h* take place in the polymer melt which is highly viscous, the stabiliser molecules must be capable of dissolving in PVC and diffusing in the melt. An effective stabiliser is a liquid or a readily fusible mixture of solid compounds. All additives to the stabiliser, which improve its spreading in the polymer or reduce the viscosity of the melt, increase the efficiency of the stabiliser, i.e. lead to a physical synergism.

This in fact explains the increased efficiency of the stabilising action of group IA and IIA metal carboxylates when they are introduced simultaneously with stearic acid[20] or certain polyols.[89]

(a) Mixtures Including the Chlorides of Coordination-Unsaturated Metals

The chlorides of coordination-unsaturated metals ($ZnCl_2$, $CdCl_2$, $PbCl_2$, $FeCl_2$, $FeCl_3$, $SnCl_2$, $SnCl_4$, and R_nMCl_{4-n}, where R = alkyl or aryl, M = Sn or Pb, and n = 1–3 as well as others), having low-lying unoccupied orbitals, greatly increase the stabilising activity of compounds in the first group of stabilisers (for example, organic phosphites,[20,71] epoxy-compounds,[98] organosilicon and organogermanium hydrides,[88] and oligosilanes[75]), forming synergistic mixtures with them.

The chlorides of coordination-unsaturated metals themselves exert a complex influence on the dehydrochlorination of PVC, which depends on the concentration of the additive and decomposition time. With increased concentration of the electrophilic catalyst, the initial rate of thermal decomposition of the polymer rises.[56,60,61]

The optimum concentrations of metal chlorides (which are as a rule low), at which the maximum synergistic effect is observed, have been found.[20,42,71,75,88,98]

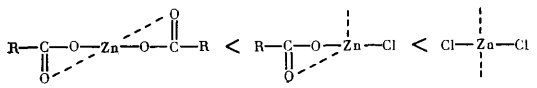
Analysis of the kinetics of the thermal decomposition of PVC in the presence of the synergistic mixtures considered, as well as the study of reactions with model compounds,[42,71,75,88,98,99,102,104] make it possible to conclude that the metal chlorides catalyse the interaction of the stabilisers in the first group with the unstable fragments of the macromolecules and with the double and conjugated double bonds (Scheme 1, reactions *b–f*).

Metal chlorides which do not behave as Lewis acids do not form synergistic mixtures of this kind.[42,71,75,88]

(b) Mixture of Other Compounds of Coordination-Unsaturated Metals with Organic Stabilisers

Synergistic mixtures with organic stabilisers (organic phosphites, epoxy-compounds, aminocrotonic acid esters, oligosilanes) are also formed by the carboxylates of coordination-unsaturated metals (zinc, cadmium, and dialkyltin),[20,34,42,69,71,75,99] organotin compounds (Ph_4Sn, trialkyl- and triaryltin isocyanates, and others),[20,86] and organolead compounds (Ph_4Pb and triphenyl-lead isocyanate).[87] The carboxylates of alkali and alkaline earth metals do not form synergistic mixtures with organic stabilisers.[20,34,42,69-71]

Mixtures of the above compounds of coordination-unsaturated metals with organic stabilisers are more effective than the mixtures with the corresponding metal chlorides[20,34,42,69,71,75] apparently because these compounds themselves stabilise PVC. Furthermore, as a result of the interaction of the metal compounds with HCl and with the unstable fragments, mixed chlorides are formed which are weaker catalysts of the thermal decomposition of the polymer than the metal chlorides. For example, the zinc salts can be arranged in the following sequence in terms of their catalytic activities:



Thus the reactivity of the zinc salt as a catalyst increases as the coordination sphere of the metal is opened.

(c) Mixtures of Zn–Ca and Cd–Ba Carboxylates

The mechanism of the synergistic action of a mixture of zinc and calcium carboxylates has been investigated.[89,99,105] As a consequence of the exchange reaction between the calcium carboxylate and $ZnCl_2$, a powerful catalyst of the dehydrochlorination of PVC is removed and zinc carboxylate, which readily enters into a nucleophilic substitution reaction with the unstable fragments of the macromolecules, is reformed.[99,105]

Calcium and zinc carboxylates form complexes with one another[99,105] and with zinc and calcium chlorides (mixed complexes).[99] The catalytic activity of $ZnCl_2$ in these complexes is reduced.[99]

Zinc carboxylates react also with the normal units of PVC, accelerating their decomposition, while calcium carboxylates diminish the rate of this reaction probably because the salts form complexes with one another.[89]

A study of the thermal decomposition of PVC in the presence of a synergistic mixture of cadmium and barium carboxylates established[70] that initially mainly $CdCl_2$ is formed (up to 90%), although the starting amounts of barium and cadmium carboxylates were identical. In the presence of barium stearate, cadmium chloride does not accelerate the decomposition of PVC, which suggests the formation of a complex between $CdCl_2$ and the barium salt.[70]

It was shown above that the synergistic effect is observed when individual stabilisers of the first and third groups are employed jointly. We shall consider synergistic mixtures in which the second component is not a stabiliser.

(d) Mixtures of Carboxylates of Coordination-Unsaturated Metals with Compounds Containing the OH, SH, and NH Groups

Mixtures of polyols with the carboxylates of coordination-unsaturated metals (Group IIB, III, and IV metals) exhibit an appreciable synergistic effect on the processes occurring in the thermal decomposition of PVC.[89-96] In their presence the rate of dehydrochlorination falls during the period T to the rate of decomposition of PVC *in vacuo*, an appreciably smaller insoluble fraction is produced, and the polymer does not become coloured.[89-91] As an example, Fig. 5 presents the dependence of the period T on the concentration of polyols in the presence of zinc and cadmium stearates.

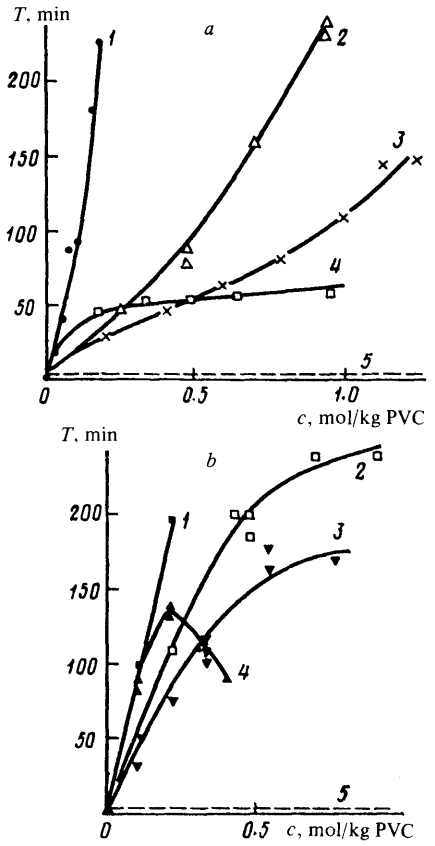
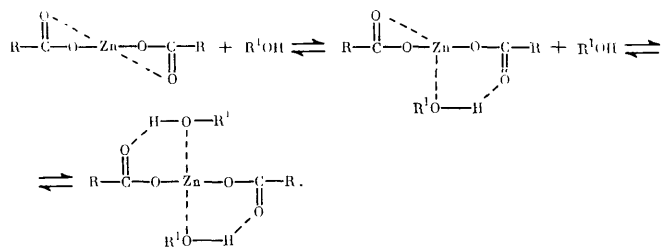


Figure 5. Dependence of the period T on the concentration of polyols in the thermal decomposition of PVC at 453 K in the presence of zinc stearate at a concentration of 0.1 mol/kg PVC (*a*) or cadmium stearate at a concentration of 0.05 mol/kg PVC (*b*).[89] *a*: 1) pentaerythritol; 2) ethylene glycol; 3) stearyl alcohol; 4) triethylene glycol; *b*: 1) glycerol; 2) ethylene glycol; 3) octyl alcohol; 4) triethylene glycol; the dashed lines represent the theoretical curves plotted assuming the additivity of the effects of the mixture components (curves 5).

The efficiency of the synergistic action of the mixtures diminishes in the following sequence: polyols > triols > diols > aliphatic alcohols; zinc carboxylate > cadmium carboxylate > tin(II) carboxylates > aluminium carboxylate.

The following observations have been made as regards the effect of mixtures of polyols with zinc and cadmium carboxylates on the thermal decomposition of s-BuCl, a low-molecular-weight compound modelling the normal fragments of the polymer:[89-91] (1) the polyols greatly reduce the rate of reaction of the carboxylates of coordination-unsaturated metals with the normal PVC unit; (2) the thermal decomposition of PVC in the presence of a mixture of carboxylates of these metals with polyols involves the exchange of a chlorine atom in the chlorine-containing groups of the polymer not only for the carboxy-group of the salt but also for the alcoholic residue; (3) salts of coordination-unsaturated metals also catalyse the addition of polyols to the double (conjugated double) bonds; (4) the polyols inhibit the catalytic effect of the chlorides of coordination-unsaturated metals on the thermal decomposition of PVC and s-BuCl; (5) among the large number of oxygen-, sulphur-, and nitrogen-containing compounds capable of forming donor–acceptor complexes of the *nV* type with zinc salts, only those containing the OH, SH, and NH groups respectively give rise to effective synergistic mixtures with zinc carboxylates.

The results can be explained by the fact that the carboxylates of coordination-unsaturated metals and compounds with the OH, SH, and NH groups form complexes having a cyclic structure (resembling chelates):



It is known that chelate complexes have a higher thermal stability and are chemically more reactive than complexes with a non-chelate structure.[106]

The formation of six-membered cyclic complexes between the carboxylates of coordination-unsaturated metals and polyols results in a considerable decrease of the rates of reaction of metal carboxylates with the normal units of the macromolecules.[89-91] At the same time, the complexes retain a high reactivity towards the active unstable fragments of the macrochains (Scheme 1, reactions *b*–*f*).

A definite contribution to the synergism of the action of the coordination-unsaturated metal carboxylate–polyol mixtures comes also from the formation of complexes by the polyols with the chlorides of the same metals.[81,89-96]

Group I and IIA metal carboxylates do not form complexes with *n*-electron donors and do not give rise to mixtures with polyols exhibiting a synergistic activity like the mixtures of polyols with coordination-unsaturated metal carboxylates.[89-96]

Certain polyols, for example diethylene and triethylene glycols give rise to an antagonistic effect with the carboxylates of Group I and IIA metals (Li, Na, Mg, Ca, Sr, and Ba). These polyols can probably act like crown-ethers, shielding the cations and enhancing the nucleophilicity of the anion, which accelerates the decomposition of PVC via the anionic mechanism:[89]

$$CaSt_2 + n\text{TEG} \rightarrow St^-[Ca\cdots n\text{TEG}]^{2+}St^-,$$

where TEG = triethylene glycol and St = stearic acid residue.

Ternary mixtures, for example, zinc carboxylate–calcium carboxylate–polyol and cadmium carboxylate–barium carboxylate–polyol, exhibit a still greater synergistic effect than the binary mixtures of components (Fig.6).[89] In their presence the rate of accumulation of ionic chlorine is lower than in the decomposition of the polymer without additives *in vacuo*. In the ternary mixture the catalytic activity of zinc salts in relation to the normal units of PVC is reduced still further compared with the binary mixtures, which has been demonstrated by model reactions with s-BuCl.[89]

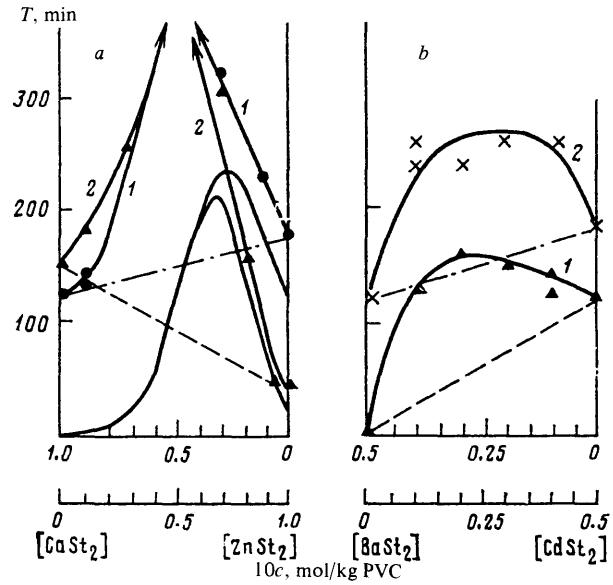


Figure 6. Dependence of the period *T* on the calcium stearate/zinc stearate (*a*) or barium stearate/cadmium stearate (*b*) molar ratio in the thermal decomposition of PVC at 453 K in the presence of polyols (mol/kg PVC):[89]
a: 1) 0.15 pentaerythritol; 2) 0.23 ethylene glycol;
b: 1) 0.1 stearyl alcohol; 2) 0.56 octyl alcohol; the dashed lines represent the theoretical curves plotted assuming the additivity of the effects of the mixture components; the thin continuous lines without symbols represent the limits of the region in which the white colour of PVC is retained.

3. Characteristic Features of the Reactions between the Stabiliser and PVC

We shall now consider the characteristics of the reactions between the stabiliser and the unstable fragments—the double (conjugated double) bonds in PVC.[107]

1. Compounds of coordination-unsaturated metals (Sn, Pb, Zn, Cd, Sb, etc.) participate in nucleophilic substitution reactions of the unstable fragments of PVC macromolecules. Compounds of these metals enter into the composition of the most effective PVC thermostabilisers.

2. The PVC melt (433–473 K) containing the added stabiliser is a dielectric with a low electrical conductivity and the formation of ions in such a system is unlikely. In terms of the classification of nucleophilic substitution reactions adopted in organic chemistry[8] the reactions of PVC with the stabiliser can be classified as belonging to the class of S_N2 bimolecular nuclophilic substitution reactions, subject to the stipulation that the reaction proceeds not between the anion and an alkyl chloride but apparently in a complex of the CTC

type, where the donor is the polymer fragment and the acceptor is the compound of the coordination-unsaturated metal.

3. It has been shown on model compounds that fragments containing chlorine in the allyl position and at the branching points are much more reactive in nuclophilic substitution reactions than the normal chain units. The large difference between the rates of these reactions makes it possible to select a compound of the coordination-unsaturated metal such that at 443–473 K it hardly interacts with the normal PVC units but reacts rapidly with the labile groups. All the effective PVC stabilisers satisfy this condition.

4. The nuclophilic substitution reaction is complicated by the elimination of HCl. The rate of the elimination reaction is determined by the electrophilic properties of both the initial components of the stabiliser and those of the products of their interaction with HCl and the chlorine-containing PVC fragments. Coordination-unsaturated metal chlorides accelerate the reaction of the stabiliser with the chlorine-containing fragments and the HCl elimination reaction.

5. Complex-forming agents containing O, S, N, and P atoms and forming complexes with compounds of coordination-unsaturated metals influence the rates of nucleophilic substitution and HCl elimination reactions. The best stabilising effects are attained when compounds having several OH, SH, and NH groups are used.

6. The rate of reaction between the stabiliser and PVC is lower than the rate of its reaction with the low-molecular-weight model compound, which apparently can be accounted for by the high viscosity of the polymer melt and the complication of the process by diffusion phenomena.

7. Whereas the nucleophilic substitution reactions are being vigorously investigated and they explain the mechanism of action of the majority of stabilisers, the reactions of the stabilisers with double and conjugated double bonds have been inadequately studied. At the same time, polyenes exhibit an increased reactivity at elevated temperatures (440–480 K): they participate in intramolecular and intermolecular reactions with liberation of benzene and the formation of a cross-linked polymer. The catalytic action of HCl is associated with its reversible addition to polyenes (reactive intermediate species, namely the ion pairs formed in this reaction, accelerate the thermal decomposition of PVC).

The steric structure of the polyenes should play a major role: dienophiles should interact only with *cis*-dienes, benzene can be formed only in the presence of triads of conjugated double bonds with a specific steric structure, etc.

The increased stabilising effect of many synergistic mixtures of compounds of coordination-unsaturated metals with substances containing the OH, SH, and NH groups as well as other organic compounds is associated with the increase in the rates of reactions involving electrophilic addition to double and conjugated double bonds.

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The Deposition of Epitaxial Layers from the Vapour of Organometallic Compounds

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Different methods of depositing epitaxial layers from the vapour of organometallic compounds have been compared. The stability of the deposition processes and new data on the preparation of epitaxial layers of $A^{III}B^{V}$, $A^{II}B^{VI}$, and $A^{IV}B^{VI}$ compounds have been examined.
The bibliography contains 206 references.

CONTENTS

I. Introduction 770
II. Comparative characteristics of methods of deposition from the vapour of organometallic compounds 770
III. Deposition of epitaxial layers of $A^{III}B^{V}$ compounds 775
IV. Deposition of epitaxial layers of $A^{II}B^{VI}$ and $A^{IV}B^{VI}$ compounds 776

I. INTRODUCTION

In the nineteen-twenties, Razuvaev[1] studied the thermal decomposition of organometallic compounds (OMC) in a stream of hydrogen. Later, work by Paneth[2-6] drew attention to alkyl compounds of the transition metals as sources of free radicals in the gas phase at pressures of ~10^{-3} mmHg. Subsequently, Razuvaev and co-workers[7-9] showed that alkyl and aryl OMC act as sources of radicals in the liquid phase. Later, Razuvaev's school studied the mechanism of the decomposition of alkyl and aryl OMC of zinc,[10-12] cadmium,[13-15] mercury,[16-20] germanium,[21-23] tin and lead,[24-32] indium,[33] aluminium,[34-36] and antimony,[37] and a number of other compounds. These studies dealt with both the reactions of the radicals and the formation of metallic phases; by 1960 they had provided a theoretical basis for the study of the deposition of epitaxial layers of binary and multicomponent semiconductors using OMC, an intensively developing field of present-day materials science.

In 1959 it was found that the reaction of trimethylantimony with diborane gives a deposit with the composition BSb_x and gaseous methane.[38] It was subsequently shown[39] that the reaction of trimethylindium with phosphine takes place in three stages:

$$InMe_3 + PH_3 \xrightarrow{-100^\circ C} InMe_3 \cdot PH_3 \xrightarrow{-80^\circ C} (MeInPH)_n \xrightarrow{300^\circ C} InP$$

and that the reactions of trimethylgallium (TMG) with arsine and of trimethylindium with stibine take place according to the schemes:[40]

$$GaMe_3 + AsH_3 \xrightarrow{28^\circ C} \text{grey film} \xrightarrow{200^\circ C} \text{red film} + CH_4$$

$$InMe_3 + SbH_3 \xrightarrow{28^\circ C} (MeInSbH)_n \xrightarrow{160^\circ C} InSb + CH_4 .$$

The practical application of the alkyls of the elements of groups II and III of the periodic system began, however, after the development of the technology of the deposition of epitaxial layers in 1968, when the reaction of TMG with arsine was proposed for the preparation of epitaxial layers of gallium arsenide.[41] In subsequent years, the reactions of the alkyls of the group III elements with ammonia, the hydrides of phosphorus and arsenic, and antimony alkyls were proposed for the preparation of epitaxial layers of the compounds GaAs, GaP, $GaAs_xP_{1-x}$, and $GaAs_xSb_{1-x}$ and the ternary semiconducting compounds $Ga_{1-x}Al_xAs$,[42-45] aluminium phosphides,[46] aluminium and gallium nitrides,[47] indium arsenide and phosphide, and the ternary systems $Ga_xIn_{1-x}As$ and $InAs_xP_{1-x}$,[48] and epitaxial layers of $A^{II}B^{VI}$ compounds.[49,50] The hetero-epitaxial deposition of $A^{II}B^{VI}$ and $A^{III}B^{V}$ layers was reviewed in 1971.[51] Subsequently, the preparation of films by the reactions of alkyls of group IV elements with the hydrides and alkyls of group VI elements ($A^{IV}B^{VI}$ compounds) was described,[52] a number of patents on the preparation of epitaxial structures and hetero-structures by the reactions of OMC with hydrides appeared,[53-56] and the method began to be called the OMC–hydride process†.

Most work has been devoted to the deposition of epitaxial layers of $A^{III}B^{V}$ compounds, because of their widespread use in opto- and micro-electronics. Work on the development of epitaxial $A^{II}B^{VI}$ layers has begun to develop only since 1978, because of the difficulty of obtaining and alloying these compounds. At the same time, the theory of the deposition of epitaxial layers from OMC vapour has been developed, and this is reflected in a number of monographs[57,58] and reviews on the preparation of $A^{III}B^{V}$ [59-63] and $A^{II}B^{VI}$ [64,65] compounds. Except for Ref.65, where data on the thermal decomposition of various OMC in a stream of hydrogen were examined, most reviews have dealt with the preparation of hetero-structures for the production of electronic instruments, and the study of their properties. The present review examines the relationship between the mechanism and kinetics of the reaction and the stability of deposition processes, and discusses the latest data on the preparation of epitaxial layers from the vapour of OMC.

II. COMPARATIVE CHARACTERISTICS OF METHODS OF DEPOSITION FROM THE VAPOUR OF ORGANOMETALLIC COMPOUNDS

Methods of deposition from the vapour of OMC can be classified according to two main characteristics: the compounds used to transport the elements into the reactor, and the deposition conditions. In any method, the deposition from the vapour phase takes place via a number of

†In the foreign literature this method is called the MOCVD method—Metalorganic Chemical Vapour Deposition.

intermediate stages: I) volatilisation of the original compounds, II) mixing and transport of the starting materials, III) diffusion of the vapour of the starting materials to the support, IV) adsorption, V) reaction or thermal decomposition, VI) crystallisation of the epitaxial layer, and VII) removal of gaseous products from the reactor.

Three main methods of transport are used in deposition from the vapour of OMC. Thus binary compounds AB are obtained by the reaction:

$$AR_n(\text{gas}) + BR'_m(\text{gas}) \rightarrow AB(\text{crystalline}) + X(\text{gas}) \quad (1)$$

where n, m = 1, 2, 3, 4; A is an element from groups II, III, or IV, B an element from groups V or VI, R an alkyl group, R′ a hydrogen atom or an alkyl group, X the gaseous products of reaction (1), and (crystalline) and (gas) denote the condensate and the gas phase. In stages IV and V, reaction (1) can take place with the formation of intermediate polycondensed products with the formula $(-R-A-B-R')_n$, as observed for the reaction of TMG with arsine,[66] so that complexes of the type $AR_n.BR'_m$ are used for the deposition of binary semiconducting structures.[67]

A completely different method of transport involves the use of organobimetallic compounds containing an A–B bond.[68–72] Cadmium sulphide,[68] layers of titanium,[69] and epitaxial layers of $A^{IV}B^{VI}$,[70–72] $A^{II}B^{VI}$, and $A^{III}B^{V}$[73] compounds have been prepared. The use of molecular complexes and organobimetallic compounds makes it possible to reduce the synthesis of a complex semiconducting compound to the preparation of elementary semiconductors, but the stoichiometry and electrical properties of the layers can be controlled only by selecting the temperature and pressure, since the ratio of the reagents A and B is fixed in the original compound.

Depending on the conditions, deposition from the vapour of OMC is carried out by vacuum methods or by methods involving a carrier gas. Historically, methods of vapour-phase deposition based on the transport of the elements or chlorides using hydrogen[74] were transferred, by replacing the chlorides by OMC, to the deposition of epitaxial layers of binary compounds from the vapour of OMC. The process is carried out as follows: the carrier gas, usually hydrogen, is passed through bubblers in which it is saturated by the vapour of the OMC, and then through tubes into the reactor in which the epitaxial layer is deposited. Up to 12 material supply channels are used simultaneously. If a homogeneous reaction between the original compounds is impossible, they are mixed beforehand; if the reaction is possible, they are injected into the reaction zone. The carrier gas is used at atmospheric pressure or at a reduced pressure.[75]

The carrier gas is used as a reference defining the pressure in the deposition system, and makes it possible to transfer precise quantities of the original OMC and to control their supply automatically; this is particularly important in the production of multicomponent structures.

At the same time, the use of a carrier gas has a negative effect on the properties of the layers obtained, because of hydrogen etching of the growing layer, the concentration of impurities from the carrier gas in the epitaxial layer, the transfer of droplets and particles from the volatiliser to the reactor, and the increased difficulty of removing the reaction products. OMC displace light gases from an adsorption layer,[76,77] but since the relative concentration of the reagents does not exceed 1–2 vol.%, the carrier gas nevertheless blocks the adsorption centres, leading to energetic uniformity of the growth surface and hence to a corresponding decrease in the proportion of selective decomposition of the OMC.[78]

Vacuum methods of deposition from the vapour of OMC in the absence of a carrier gas have now been developed.[57,58] This method has been used to obtain epitaxial layers of $A^{IV}B^{VI}$,[72] $A^{III}B^{V}$,[79–82] and $A^{II}B^{VI}$[83–88] compounds. An attempt has been made[89] to obtain GaAs from arsine and TMG vapour under molecular-beam epitaxy conditions; arsine had previously been used as a source of arsenic in molecular-beam epitaxy.[90] In vacuum methods, the purity of the layers obtained is determined by the purity of the OMC and hydrides used, in which the concentrations of metal and non-metal impurities are 10^{-4}–10^{-5} vol.%. Hydrogen purified by diffusion through a palladium membrane contains up to 4×10^{-5} vol.% of oxygen-containing impurities.[91] The proportion δ of impurities in the layer can be determined from the relationship

$$\delta = \frac{j_i}{j_0}\frac{k_i}{k_0}$$

where j_i and j_0 are the fluxes of the molecules of the impurity and the OMC at the growth surface, and k_i and k_0 the coefficients of reactive adhesion of the impurity and the OMC.

The capture of oxygen-containing impurities in an epitaxial layer can be examined for the case of the deposition of $Ga_{1-x}Al_xAs$ from the vapour of TMG, trimethylaluminium (TMA), and arsine.[91,92] The hydrogen stream contained less than 1 vol.% OMC, and comparison of the rates of deposition given by the authors cited and estimation of the fluxes of the OMC into the adsorption layer indicate that for TMG and TMA, the value of k_0 is 1–0.01, whereas $k_i \cong 1$, since the OMC is a compound which is rapidly oxidised. Thus the concentration of aluminium and gallium oxides in the epitaxial layers can apparently reach several tenths of 1%. With decrease in the hydrogen pressure, therefore, layers of high quality are obtained at lower deposition temperatures than at atmospheric pressure.[75] Decrease in pressure facilitates the effective removal of the gallium oxide decomposition products from the reaction zone. This is confirmed by data[92] which show that at a concentration of oxygen-containing impurities in the hydrogen stream at the level of 10^{-6} vol.%, the $Ga_{1-x}Al_xAs$ layers with $x < 0.05$ were of high quality, whereas at $x > 0.05$ the conductivity and photoluminescence yield of the layers decreased sharply, since aluminium oxides are stable under the deposition conditions.

The thickness of the oxide on the $Ga_{1-x}Al_xAs$ surface is proportional to the value of x,[93] and layers of high quality are obtained only after the hydrogen has been specially purified from oxygen-containing impurities.[91] In deposition in a vacuum, the purity of the layers is determined by the purity of the OMC and the ratio of the flux corresponding to the leakage from the atmosphere into the reactor to the flux of the starting materials into the reactor. At a level of leakage into the reactor lower than the sensitivity of the helium leak detector, and fluxes of the original reagents into the reactor of ~10 litre mmHg s^{-1}, the concentration of oxygen-containing impurities due to leakage into the reactor is not more than 10^{-9} vol.% (without allowance for the absorption of oxygen and water vapour by the walls of the reactor and by the reaction mixture).[79]

In deposition under the conditions of molecular-beam epitaxy, the pressure of the residual gases in the reactor is 10^{-10} mmHg, and the fluxes of the atoms on to the growth surface corresponds to pressures of 10^{-5} mmHg, so that the purity of the layer with respect to the impurities present in the residual gases is 10^{-3} vol.%. The use of improved evacuation techniques will be unlikely to lower significantly the level of contamination of layers obtained in this way due

to residual gases, since at low pressures of the original reagents in the reactor, the atomically pure surface of the growing crystal actively captures impurities.

The mechanisms of the reactions taking place in the adsorption layer depend on its density and the quantity F, equal to the ratio of the energy of intermolecular interaction in the adsorption layer to the energy of the interaction of the adsorbed molecules with the surface. At a low density of molecules in the adsorption layer, $F \ll 1$, the original reagents react with the surface of the support, and a vapour–crystal (VC) growth mechanism is realised. At a medium density of the adsorption layer and a value of $F \cong 1$, the formation of surface compounds which can play the role of liquid is possible, and in addition to the VC growth mechanism, the vapour–liquid–solid (VLS) growth mechanism may be observed. At a high density of the adsorption layer, the value of $F \gg 1$; growth of the layer takes place by the VLS mechanism, drops of liquid are generated from the original elements on the surface, and metastable phases, polymer chains containing metal, carbon, and hydrogen, may be formed.

These relationships can be illustrated by the reaction of TMG with arsine. The reaction of TMG with arsine takes place via the formation at 203° of co-condensation products Me_2–Ga–As–H_2, which at 259° decompose with the liberation of condensation products $(Me–Ga–As–H)_n$, which subsequently decompose at 420 °C with the liberation of gallium arsenide.[66] A study of the deposition of gallium arsenide from arsine and TMG vapour at a hydrogen pressure of 75 mmHg[75] showed that an amorphous deposit with a thickness of up to 500 Å remains on the surface of the epitaxial layer; the photoluminescence spectrum of this deposit showed a weak broadened band at 1.37 eV, and the edge band appeared only after this surface amorphous layer had been etched; the layer was apparently formed by residues of the co-condensation products of TMG and arsine, involved in the growth of gallium arsenide. In the deposition of gallium arsenide in a vacuum,[80] at Knudsen numbers (Kn) in the flux of arsine and TMG vapour of 1–0.1, no residual products were observed on the surface of the films. At Kn ≅ 1 and a deposition temperature of 400°, block single-crystal layers were obtained; the epitaxy temperature was 430°, as in deposition by the method of molecular-beam epitaxy; at temperatures above 500°, highly perfect layers were obtained. At Kn ≅ 0.1, the epitaxy temperature increased to 500°, corresponding to the regular features observed in deposition in a stream of hydrogen at a reduced pressure.

A study of the defects in gallium arsenide layers obtained by deposition in a vacuum[82] showed that the films deposited at Kn ≅ 1 had a rough surface, on which drops with dimensions of up to 300 Å were observed; the principal defects were dislocations, twins, and subtractive packing defects. As Kn → 0, the size of the droplets increased to 1500 Å with an increase in the density of defects, followed by a sharp change to the growth of layers with an atomically smooth surface and minimum density of defects, in spite of the fact that the concentration of p-type carriers in the film reached 10^{19}–10^{20} cm^{-3}. This change in the properties of the layer with increase in the pressure at which the deposition was carried out can be attributed to a change in the growth mechanism from VC to VLS; the agent forming the liquid on the surface of the growing layer may be the intermediate compound considered above.

The characteristic features of the alloying of gallium arsenide with selenium are also related to the mechanism of the reaction in the adsorption layer. Thus when hydrogen selenide is introduced into the stream,[82] highly compensated specimens of n-type gallium arsenide are obtained, and the morphology of the surface and the concentration of defects correspond to the picture observed in the growth of layers with an excess of TMG, that is the introduction of a small quantity of selenium into the adsorption layer facilitates the "attraction" of TMG molecules, revealed in the apparent displacement of the conductivity conversion point. These data agree with the results of published work[94] where displacement of the conductivity conversion point was observed in the deposition of gallium arsenide from TMG and arsine with change in the concentration of impurities in the TMG.

The purity of binary semiconducting layers is determined to a large extent by the stoichiometry, since impurities are captured preferentially on the vacancies. This is illustrated by the deposition of layers of zinc selenide by the reaction of diethylzinc (DEZ) and hydrogen selenide.[85,88] Small quantities of ethyl iodide were introduced into the DEZ to a concentration of 0.01–1 vol.%. During the deposition, the temperature of the support was 350°, and the pressure in the reactor 0.2 mmHg. Zinc selenide was deposited by the reaction

$$ZnEt_2 + H_2Se \rightarrow ZnSe + 2EtH \qquad (2)$$

accompanied by the thermal decomposition of DEZ, which takes place vigorously at temperatures above 300°,[95,96] while zinc reacts with hydrogen sulphide according to the equation

$$Zn + H_2Se \rightarrow ZnSe + H_2 .$$

In the presence of an alkyl iodide, however, the zinc atoms can react with it to form the intermediate compound Et–Zn–I,[97] which undergoes symmetrisation to give DEZ and zinc iodide; the synthesis of DEZ from zinc and an alkyl iodide takes place up to 380°,[98] and the symmetrisation of the intermediate compound EtZnI is the limiting stage.[99]

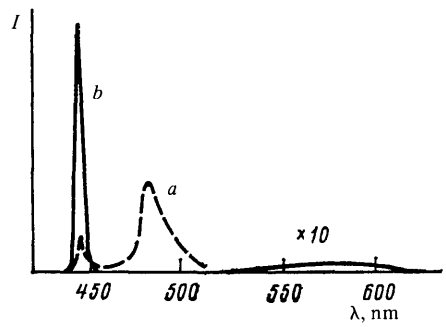

Figure 1. Photoluminescence spectra of zinc selenide layers; ratio of the fluxes of DEZ and hydrogen selenide 1 : 2 (*a*) or 1 : 5 (*b*).

Reaction (2) is rapid, so that the thermal decomposition of DEZ is possible only when there is an excess of it in the adsorption layer;[93] in this case, in the presence of an alkyl iodide, the compound EtZnI is formed and then decomposes to give Zn–I· radicals. The condensation of this radical leads to the capture of an iodine atom on a selenium vacancy in zinc selenide. Thus the photoluminescence spectrum of zinc selenide specimens obtained at a ratio of the DEZ flux to the hydrogen selenide flux into the reactor of 1 : 2 (Fig.1*a*), in addition to the edge band, shows a peak

at 480 nm, corresponding to an iodine donor level, and with change in the ratio of the fluxes of DEZ and hydrogen selenide to 1:5, the intensity of this peak decreases by a factor of 300[88] (Fig.1*b*). Thus the capture of the iodine impurity is due to the thermal decomposition of DEZ and the formation of EtZnI intermediate compounds, and the observed displacement of the iodine impurity by the growing crystal front is due to the suppression of the synthesis of the compound containing the Zn–I bond. The characteristics of the methods of molecular-beam epitaxy, deposition from OMC vapour in a vacuum, and the OMC–hydride process in a stream of hydrogen are compared in Table 1.

Table 1. Comparison of the characteristics of the methods of molecular-beam epitaxy and the OMC–hydride process in a stream of hydrogen and in the absence of a carrier gas.

Method	γ*	Desorption	LSC**	Growth mechanism	Deposition conditions
Molecular-beam epitaxy	10^{-5}	fast	attainable	VC	supersaturation rigidly related to the flux; removal of products not limited by diffusion
OMC-hydride process in hydrogen	10^{-7}–10^{-2}	blocked	not attainable	VLS	supersaturation depends on the reagent fluxes; removal of products limited by diffusion
OMC-hydride process without a carrier gas	up to 10^{-10}	fast	attainable	VC or VLS	supersaturation depends on the reagent fluxes and the pressure in the reactor; removal of products not limited by diffusion

*Ratio of the sum of the fluxes due to leakage into the reactor, residual gases, and impurities in the carrier gas to the flux of the original reagents reaching the support.
**Local stability of the concentrations.

The differences between the epitaxy processes in a vacuum and in a stream of carrier gas are considerable, particularly in stages III, IV, and VII. The carrier gas, which brings about the transport of the OMC from the volatilisers into the reactor, simultaneously acts as measurement reference for determining the pressures of the components in the stream. For deposition in a vacuum, this reference is not available, and this creates a number of difficulties in the control of the fluxes and the stabilisation of the deposition conditions, and requires examination of the dynamic process as a whole.[57,58]

The gas-dynamic conditions in the reactor when a carrier gas is used are traditionally studied by introducing an aerosol into the gas stream;[100] the aerosol particles, however, do not detect the fine swirling movements which are detected by interferometry. The gas dynamics of reactors of different design have been studied using a Mach–Zehnder interferometer.[101] The results of the study of the gas dynamics of horizontal reactors have been reviewed.[102] The relationship between the development of the growth surface and gas-dynamic factors has been studied.[103–105]

At pressures below 20 mmHg, schlieren and interferometric methods are not effective, so that indirect methods have to be used to study the flow of the vapour on to the support. The simplest method is to study the profile of the deposited layer, or to record the temperature and pressure profiles in the vapour stream. The reaction of DEZ with hydrogen selenide is used to make visible the flow picture at pressures of $10–10^{-3}$ mmHg.[106] The layer of zinc selenide deposited on a probing plate makes it possible to obtain a detailed picture of the flow on to the support from the tarnish iridescence colours, and the luminescence of the layer can be used to study the mixing of the streams when they are injected into the reactor and the separation into layers of components with different molecular weights.

The vacuum systems for epitaxy from OMC vapour consist of four main units: the volatiliser, the reactor, the traps, and the evacuation system; they operate in the pressure range 10^{-2}–5 mmHg, where viscous gas flow conditions are replaced by molecular flow conditions, and are characterised by a high degree of conversion of the original reagents. The diffusion of the OMC to the support takes place through a layer of reaction products diffusing in the opposite direction, and a complex relationship is established between the reaction rate, the pressure in the reactor, and the thickness of the "reduced" film. The rate of evacuation of the products from the reactor, the rate of the supply of the OMC vapour to the reactor, and the degree of transformation in the reactor are also related in complex fashion. Overall, however, the process of deposition from OMC vapour in a vacuum is autonomous.

The theory of dynamic vacuum systems for deposition from OMC vapour has developed comparatively recently, since 1967. Thus the fluctuations in the growth rate as a result of competition between stages III and VII have been examined.[107] According to the proposed model, binary diffusion of the OMC and the thermal decomposition products takes place in the "reduced" film, and the rate of removal of the reaction products from the reactor is of the same order of magnitude as the rate of binary diffusion. In this case, fluctuations in the concentrations of the OMC and the decomposition products can take place in the reactor, and the frequency of the fluctuations is related to the reaction rate constant, the rate of evacuation, and the geometric parameters of the reactor. Analysis of the model for stability of the stationary deposition conditions showed that the higher the rate of pumping and the smaller the mass-transfer constant in the reduced film, the higher the probability that fluctuational conditions will be established; the frequency of the fluctuations increases with increase in the rate of pumping, and decreases with increase in the mass-transfer coefficient to the surface of the support. The fluctuations in the concentrations of the OMC and the thermal decomposition products lead to non-uniformity of the composition of the film along its thickness and to the growth of layer structures.

A model of acoustic self-fluctuations in the density of the vapour in the reactor, brought about by the transfer process at the start of the deposition, has been examined.[108] In the approximation of a differential reactor, with simplifying assumptions about the pressure and temperature profiles, it was shown for the case of viscous flow in a long cylindrical reactor that the acoustic wave produced when the OMC vapour is introduced into the reactor is reflected, returns to the support, and induces a change in the OMC concentration at the support. At certain ratios of the reaction rates, the geometric parameters of the reactor, and the vapour pressure in the system, sustained fluctuations of the density are excited, and their energy is supplemented by the liberation of gas during the thermal decomposition.

The self-fluctuations in the rate of growth of a film due to thermal phenomena such as the finite nature of the rate of heat transfer from the heater to the surface of the support

and the absorption or liberation of heat in the reaction on the surface have been studied.[109] If the thermal decomposition of the OMC is endothermic and autocatalytic, the liberation of solid products leads to an increase in the reaction rate, an increase in the rate of removal of heat, and a decrease in the temperature of the support; as a result, the degree of coverage of the surface with thermal decomposition products increases, the reaction rate decreases, the temperature of the surface increases, and the cycle is repeated. If the decomposition of the OMC is kinetically restricted (at low temperatures), self-fluctuations in the temperature of the support will be excited if the power of the heater is insufficient or if the support has a low thermal conductivity. The change to diffusion deposition conditions suppresses the self-fluctuations. Exothermic reactions also lead to the excitation of fluctuations in the temperature of the support, since the liberation of heat in the reaction leads to an increase in its rate and to "depletion" of the starting materials, the reaction rate decreases, the temperature of the surface decreases, and the cycle is repeated. A low thermal conductivity of the support leads to an increase in the amplitude of the fluctuations; the heat liberated in the reaction supplements the energy of the fluctuations.[58]

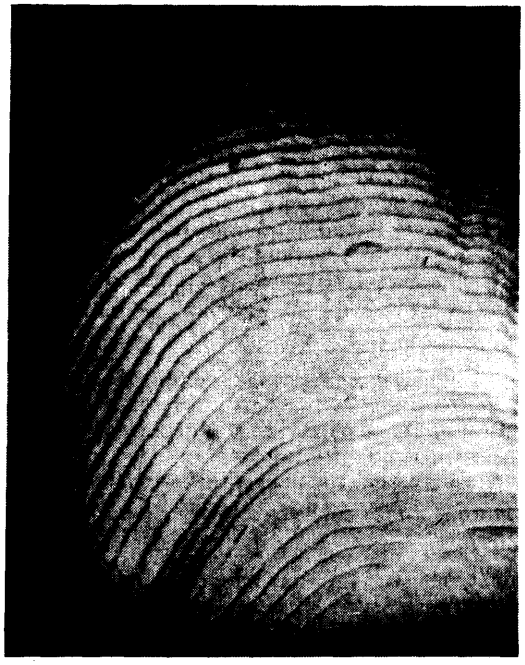

Figure 2. Transverse section of a layer of zinc selenide. Dark layers—with an excess of selenium; light layers—stoichiometric zinc selenide.[85]

The fluctuations in the pressure in the reactor and the corresponding changes in the composition of the layer being deposited have been observed experimentally; the experimental results agreed with the theory.[110,111] Essentially, all the above models relate to cases where competition between various types of mass transfer in the deposition system (stages II, III, and VII) moves the reaction from kinetic conditions to diffusion conditions or vice versa; this is a characteristic feature of deposition from OMC vapour in a vacuum, since at pressures of ~0.1 mmHg the concentrations of the OMC in the volume ($\sim 10^{15}$ cm^{-3}) and on the surface ($\sim 10^{15}$ cm^{-2}) are of the same order of magnitude. The fluctuations are suppressed when the deposition conditions move "deep" into the diffusion range, but this is not always possible, because of the influence of pressure and temperature on the quality of the deposited layer.

The fluctuations in pressure in the volatiliser–reactor–trap system, arising in the production of a binary compound AB by several parallel reactions, when the rate of the leading reaction is much greater than those of the other reactions, and when hydrogen, which is not frozen out in the trap, is liberated in the reaction products, have been examined.[112] The products of the main reaction are condensed in the trap. The highest rate of deposition corresponds to the growth of the stoichiometric layer AB, the graph giving the pressure dependence of the growth rate passes through a maximum, and fluctuations of pressure in the reactor should be excited at a certain critical pressure and are accompanied by fluctuations in the rate of liberation of hydrogen. Fluctuational conditions of this kind were observed in the preparation of zinc selenide by the reaction of DEZ with hydrogen selenide.[85] The fluctuations in pressures were accompanied by the growth of a structure consisting of periodically alternating layers of stoichiometric zinc selenide (light layers in Fig.2) and ZnSe with an excess of selenium (dark layers in Fig.2). The frequency of the fluctuations was related to the volume of the reactor, the working pressure, and the rate of removal of the volatile component.[112]

The fluctuations in the concentrations of the components of the reaction in the adsorption layer, due to the characteristic features of the desorption and adsorption of the OMC and the phenomena of heterogeneous catalysis and development of the growth surface, have been examined.[58,113] The fluctuating change in the surface concentrations in the adsorption layer is excited by autocatalytic phenomena, the activated chemisorption of the OMC and the decomposition products, the multistage nature of the surface reaction, and the two-dimensional condensation of intermediate phases, and can take place without a change in the pressure in the reactor.

Thus methods of deposition in a carrier-gas stream have been developed technically, and make it possible to produce multicomponent mixtures of OMC and hydrides under dynamic conditions, automatically, and with a high accuracy. A high carrier-gas pressure in the deposition system makes it possible to separate stages I and II, III and VII. The quality of the layers obtained by this method is decreased by contamination by impurities from the carrier gas, etching of the growing layer, blocking of the adsorption centres by molecules of the carrier gas, the consequent decrease in the fraction of the selective decomposition of the OMC, and local instability of the concentrations, due to convective and turbulent diffusion and small-scale rotational movements in the boundary layer.

The vacuum method of deposition from OMC vapour does not have the disadvantages associated with the use of a carrier gas, and this makes it possible to improve considerably the quality of the layers and to achieve automatic control of the deposition process, finer control of the supersaturation, and stabilisation of the fluxes of the reagents to the growth surface. This method is more complicated, however, in the generation of the fluxes of the original OMC, and requires detailed experimental and design studies to

find stable deposition conditions; this is related to the use of flow conditions close to the range corresponding to the change from viscous to molecular conditions.

III. DEPOSITION OF EPITAXIAL LAYERS OF $A^{III}B^{V}$ COMPOUNDS

Epitaxial layers of binary semiconducting compounds $A^{III}B^{V}$ are obtained by the reactions of OMC and hydrides and molecular complexes. There is comparatively little published information on the mechanism of the reactions accompanying deposition. A study of the reaction of TMG with arsine[66] (see above) showed that the polycondensed fragments containing the $\rangle$Ga–As$\langle$ bond undergo autocatalytic decomposition to gallium arsenide. The homogeneous nucleation of aggregates $(GaAs)_n$,[114–116] the formation of homogeneous polymeric species containing Ga, N, C, and H atoms in the reaction of TMG with ammonia, and the formation of polymeric layers containing In, P, C, and H in the reaction of trimethylindium with phosphine[117] have been proposed, but no direct proof of homogeneous nucleation has been give.

The conditions for the distillation of the molecular complexes $ClEt_2Ga.AsEt_3$, $ClEt_2Ga.AsMe_3$, $ClEt_2Ga.NEt_3$, and $ClEt_2Ga.PEt_3$,[118] which can be used to obtain layers of $A^{III}B^{V}$ compounds, have been studied. The complex $Me_3Al.NH_3$ has been used to obtain aluminium nitride.[47] The first methane molecule is removed at 60°, and the second at 160°; decomposition to form AlN is complete at 1200°.[47,119,120] The thermal decomposition of the complexes $Cl_3Al.NH_3$ and $Me_3Ga.NH_3$ [121,122] and the decomposition of the complexes $Et_3Ga.NH_3$, $R_3Ga.AsR_3$,[123] $Me_3In.PMe_3$,[124] and $ClEt_2Ga.AsEt_3$ [125] have been studied. A number of complexes containing the Ga–As bond have been studied to obtain layers in a horizontal flow reactor in a stream of helium.[126] It was reported that the type of conductivity depends on the method used to heat the support; the authors cited consider that this was proved by the fact that the Ga–As bond is not broken, although change in the type of conductivity is due rather to a change in the type of self-alloying impurities when working with a hot or cold reactor wall. The complex $(Et_2Ga.PEt_2)_3$ has been used to obtain layers of GaP.[127] The thermal decomposition of $ClEt_2Ga.AsEt_3$ has been studied.[128] The deposition of the ternary system $GaAs_{1-x}P_x$ with values of x in the range 0–0.6 from $ClEt_2Ga.AsEt_3$ and diethylphosphine vapour has been examined.[129]

The process of deposition from OMC vapour is analysed by the method of partial pressures,[130] which involves the numerical solution of systems of equations for the partial pressures and equilibrium constants, and the subsequent construction of equilibrium diagrams on coordinates temperature–pressure–composition. These diagrams have been constructed for the system Ga–As–Cl–H; a comparison[131] of the deposition of gallium arsenide from OMC vapour with the chloride–hydride process showed that the OMC–hydride process has a wider range of conditions for the existence of gallium arsenide, makes possible a smoother control of the supersaturation, and is less critical with respect to the degree of stabilisation of the conditions of the experiment. A study of GaAs layers deposited from a mixture of the vapours of arsine and the ether addition compound of TMG, labelled in the methyl group with the ^{14}C isotope, showed that the ^{14}C concentration did not exceed 6×10^{13} cm^{-3} and agreed with the thermodynamic analysis.[132,133] A thermodynamic analysis of the system TMA–trimethylantimony showed that at the deposition temperature of aluminium antimonide (623°) the product is aluminium carbide, and that the use of tri-isobutylaluminium instead of TMA makes it possible to decrease sharply the concentration range corresponding to the synthesis of aluminium carbide,[134] and this was confirmed experimentally.[135] Subsequent work was directed towards the preparation of the ternary and quaternary systems $Ga_{1-x}Al_xSb$ and $Ga_{1-x}Al_xAs_{1-y}Sb_y$ [136] and the study of the influence of the pressure of the OMC of group III elements relative to the vapour pressure of the compounds of group V elements on the composition of the $GaAs_{1-x}Sb_x$ layers obtained; the results of the thermodynamic calculations agreed with the experimental data.[137,138]

Published data on the kinetics of the growth of $A^{III}B^{V}$ epitaxial layers from OMC vapour are obtained by recording the dependence of the rate of deposition on the parameters of the process. The rate of deposition is independent of temperature in the range 600–800°. *..... semiconducting compounds and the development of instruments based on epitaxial layers, *..... group V, and is of first order with respect to the consumption of the OMC vapour. The process is generally carried out under conditions of diffusion control, so that the rate of deposition increases with increase in the flux rate.[41,75,139]

The mechanism of the deposition of gallium arsenide by the reaction of TMG with arsine has been studied by infrared spectroscopy. Thus TMG begins to decompose in a stream of hydrogen at a temperature above 400°, and the rate of the thermal decomposition is stabilised above 600°. Arsine begins to decompose at 650°; above 750°, the degree of conversion of AsH_3 is close to 1. When TMG, arsine, and hydrogen are introduced into the reactor, the infrared spectrum of the products shows a new peak at 2080 cm^{-1}, whose intensity increases with increase in the concentration of arsine in the stream and is a maximum in the temperature range 510–550°.[140]

Most work on the deposition of layers of $A^{III}B^{V}$ compounds from OMC vapour in recent years has been carried out in two main directions: the preparation and improvement of the properties of ternary and quaternary semiconducting compounds and the development of instruments based on epitaxial layers deposited from OMC vapour. Considerable progress has been made in these directions. Much work has been devoted to the production of lasers based on the hetero-structure $Ga_{1-x}Al_xAs$; lasers based on binary hetero-structures which operate for a long time at room temperatures, highly efficient solar batteries and batteries operating with the concentration of solar radiation,[141–144] field transistors,[145] photocathodes,[146] super-high-frequency transistors with record low noise values,[147] and a number of instruments for opto- and micro-electronics have been developed. The preparation of the quaternary system $Ga_{1-x}In_xAs_{1-y}P_y$ by the reaction of alkyl OMC with the hydrides of the group V elements with the preliminary decomposition of phosphine has been studied,[148] and this has led to the development of highly efficient semiconducting lasers in the near infrared range.[149] The ternary system $Ga_{1-x}In_xAs$ has been deposited,[150] and used to produce a number of opto-electronic instruments.[151] The systems $GaAs_{1-x}Sb_x$ [152] and $In_{1-x}Ga_xP$ with $x = 0.5$ [153] have also been prepared.

Work is continuing on the hetero-epitaxy of aluminium nitride from a mixture of the vapours of OMC, ammonia, and hydrazine on supports of silicon and sapphire for acoustic detectors.[154–156] Lasers based on $Ga_{1-x}Al_xAs$,

*Misprint in Russian text: two or more lines missing.

stable in proton fluxes,[157] layers of aluminium arsenide,[158] solid solutions $Ga_{1-x}Al_xN$,[159] and films of gallium arsenide on molybdenum[160] have also been obtained.

Intensive studies aimed at lowering the deposition temperature are being carried out[161-163] to produce epitaxial layers of high quality. The greatest success in this direction has been achieved by carrying out the reaction of TMG with arsine in a glow-discharge plasma. Thus the reaction of TMG with arsine at room temperature in the plasma of a helium discharge gave layers from which GaAs was isolated by treating with an electron beam.[164] A process has been developed for preparing a GaAs surface in the plasma of a helium discharge at 200° with the addition of HCl,[165] and layers of gallium arsenide suitable for use in instruments have been obtained.[166] The most perfect layers wer obtained at a support temperature of 400–450° and a pressure of helium vapour in the reactor of 1.5 mmHg.

Deposition from OMC vapour makes it possible to obtain sharp boundaries between layers with different compositions. Thus a superlattice has been produced[167] by alternating layers of n-$Ga_{1-x}Al_xAs$ (240 Å) with layers of unalloyed GaAs (225 Å). Study of the alloying profile in the layer showed that the lattice period (the distance between successive carrier concentration peaks) is ~250 Å, and that the mobility of the carriers is greater than the theoretical value; this opens up the possibility of producing improved devices.

Thus $A^{III}B^{V}$ epitaxial layers are obtained by deposition from OMC vapour using a wide range of compounds which ensure relatively low deposition temperatures and controlled alloy production. The use of OMC makes it possible to achieve precise control of the supersaturation, to obtain multicomponent systems, and to ensure that the parameters of the layer are constant over a wide area.

IV. DEPOSITION OF EPITAXIAL LAYERS OF $A^{II}B^{VI}$ AND $A^{IV}B^{VI}$ COMPOUNDS

Epitaxial layers of $A^{II}B^{VI}$ compounds show extensive promising possibilities for application in opto-electronic and electroluminescent instruments in the visible range of the spectrum.[168] Considerable effort has been put into the production of $A^{II}B^{VI}$ films, but success has been achieved only in recent years, when deposition from OMC vapour was used for this purpose. The ability of $A^{II}B^{VI}$ compounds to undergo self-compensation makes it possible to obtain conducting layers only with a low density of point defects, so that the deposition process presents more rigorous requirements regarding the level of purity from oxygen-containing impurities and the accuracy of the control of the supersaturation, compared with $A^{III}B^{V}$ compounds. Epitaxial layers of the chalcogenides of the group II elements are obtained from OMC vapour using reaction (1), and the reagents used are dimethylcadmium, dimethylzinc (DMZ), DEZ, sulphur and selenium hydrides, selenium and tellurium alkyls,[57,58] and heterocyclic derivatives of sulphur, selenium, and tellurium.[169] The thermal decomposition of the alkyls of the group II elements zinc[9-11] and cadmium[12-14] has been studied.

Table 2 gives published data[170-174] on the kinetics of the thermal decomposition of alkyls of the elements of groups II and VI. The thermal decomposition of DEZ and DMZ has been studied under static conditions,[170] in a stream of helium,[171] and in a high vacuum.[172] The decomposition of a mixture of DEZ and dimethylselenium has been studied.[173] In the decomposition of DEZ in a vacuum at a pressure of 10^{-5} mmHg, the following gaseous products were detected: CH_4, C_2H_6, C_2H_4, C_4H_8, and C_4H_{10}. Increase in temperature led to an increase in the yield of hydrogen, ethylene, and butene, and a decrease in the yield of ethane.[172] In the decomposition of DEZ under static conditions, the reaction was homogeneous. In addition to the gaseous products listed above, octane, octene, hexane, hexene, butane, and butene were detected. The data in Table 2 show that the activation energy increases with increase in the pressure and the proportion of the homogeneous reaction. Fig.3 gives published data[65] on the thermal decomposition of alkyls of cadmium, tellurium, and selenium in a stream of hydrogen. The temperature dependence of the deposition rate is determined entirely by the mass-transfer constants, as can be seen by comparing the curves for the decomposition of diethyltellurium (Fig.3). In the thermal decomposition of a mixture of DEZ and dimethylselenium, the limiting stage is the decomposition of dimethylselenium, and the ethyl radicals formed by the decomposition of DEZ induce the decomposition of $SeMe_2$.[173,174]

Table 2. Decomposition of zinc and selenium alkyls.

Compound	T, °C	Decomposition conditions	$\lg k = A - E_a/4.58\,T$		Refs.
			E_a, kcal mole^{-1}	A	
$ZnMe_2$	287—348	S.C.*	35.5	9.63	[170]
	250	flow, 10^{-5} mmHg	31.6	—	[172]
	230	flow, 10^{-4} mmHg	—	—	[171]
$ZnEt_2$	270—310	S.C., 10-100 mmHg	28.3	8.44	[171]
	310—340	flow, 760 mmHg	47.6	16.13	[171]
	100—300	flow, 10^{-5} mmHg	24.4	—	[172]
$ZnEt_2 + SeMe_2$	350—400	S.C., 90-330 mmHg	30.5	7.23	[173]
	350—400	flow, 760 mmHg	20.07	3.93	[174]

*Static conditions.

A method has been developed for obtaining dynamic P–T diagrams for heterogeneous OMC–support systems.[95,96] For a dynamic flow reactor a line is constructed on coordinates P, T, along which the rate of deposition of W according to the reactions

$$\text{OMC(gas)} \rightleftarrows \text{M(crystalline)} + \text{X(gas)} \qquad (3)$$

$$\text{M(crystalline)} \rightleftarrows \text{M(gas)} \qquad (4)$$

is equal to zero after allowance for the volatilisation of the metal. Here, M is the metal, and X the gaseous products. An expression has been obtained[175] for the rate of deposition for reaction (3), assuming that it takes place in three stages (III, IV, V), without allowance for volatilisation of the metal. Using the published data[175] and introducing the symbols P_{OMC} and P^0_{OMC} for the vapour pressures of the OMC close to the support and in the flow, and P_X and P_M for the pressures of the reaction products X and the metal vapour close to the support, it is possible to write the condition fulfilled on the line $W = 0$ as follows:

$$k_1 P_{OMC} - k_{-1} P_X + \alpha P_M = \alpha\gamma P^0_M \qquad (5)$$

where k_1 and k_{-1} are the rate constants of the forward and back reactions (3), α the coefficient of condensation of the metal, P_M^0 the equilibrium vapour pressure of the metal, $\gamma = P^{cr}/P_M^0$, and P^{cr} the critical supersaturation required for condensation of the metal on the support. For example, for the condensation of zinc on glass, $\gamma = 3$.[176] Condition (5) for $W = 0$ for a glass reactor, with allowance for the volatilisation of the metal, then has the form:

$$P_{OMC}^0 = \frac{3\alpha P_M^0 k_d}{\alpha + k_d}\left(\frac{1}{k_1} + \frac{1}{k_d} + \frac{1}{K \cdot k_d}\right)$$

where K is the equilibrium constant of reaction (3), and k_d the mass-transfer coefficient in the reduced film (for simplicity, it is assumed that the values of the transfer constants for OMC, M, and X are the same). At low pressures, the thickness of the reduced film is much greater than the dimensions of the reactor, and the following relationship is fulfilled on the line $W = 0$

$$\frac{R}{k_d} = \frac{\alpha\gamma k_d P_M^0}{\alpha + k_d}\left(\frac{1}{k_1} + \frac{1}{k_d} + \frac{1}{K \cdot k_d}\right) \qquad (6)$$

where R is the consumption of the OMC. It is possible to select the temperature and pressure in the reactor in such a way that the conditions $\alpha \gg k_d$ and $k_d \gg K$ are fulfilled. Eqn.(6) then takes the form:

$$\frac{R}{k_d^2} = \frac{\gamma P_M^0}{k_1} .$$

This relationship makes it possible to determine the activation energy of reaction (3). For the case of the volatilisation of the layer from the support, condition (5) takes the form:

$$k_1 P_{OMC} - k_{-1} P_X = \alpha P_M^0 . \qquad (7)$$

γ can be determined by comparing the temperatures of the volatilisation and condensation of the layer of metal and using Eqns.(5) and (7).

A detailed analysis of the influence of the conditions of the experiment on the observed activation energies of reaction (3) (without allowance for the volatilisation of the metal) has been carried out.[175]

The kinetics of the deposition of $A^{II}B^{VI}$ epitaxial layers have been studied.[177–182] The following method was used: the vapour of the alkyl of the group VI element was passed through a preliminary reactor (temperature 800°), in which the alkyl of the group VI element was converted into the corresponding hydride in a stream of hydrogen. The mixture of hydrogen, the hydride, and the decomposition products of the alkyl radicals was passed into a reactor in which the chalcogen hydride reacted with the OMC vapour. Cadmium and zinc sulphides and selenides were obtained in this way. The use of the preliminary reactor leads to the loss of the main advantage of the alkyls of the group VI elements over the hydrides, namely the possibility of mixing beforehand with OMC vapour.

Concentration of carbon in the specimens lay in the range $(4–8) \times 10^{20}$ cm^{-3} [177] or $(1–5) \times 10^{20}$ cm^{-3}.[178] The high concentration of carbon in the layers is apparently due to the capture by the growing layer of the cracking products of the alkyl radicals, and depends little on the deposition temperature. In fact, the concentration of carbon in the layers changes in the opposite sense to the rate of deposition.[178] The temperature dependence of the deposition rate shows two peaks: one at about 200°, and the second at about 550°.[177–179] Fig.4 gives the temperature dependence of the growth rate for the deposition of cadmium sulphide from a mixture of OMC vapour[177] and for condensation from a mixture of cadmium and sulphur vapour.[181] The regular features are similar; the curve obtained for condensation from the elements is displaced towards higher temperatures, because of the greater supersaturation, and in the deposition from the vapour of the OMC and the hydride, a decrease in the deposition rate is observed in the low-temperature range.

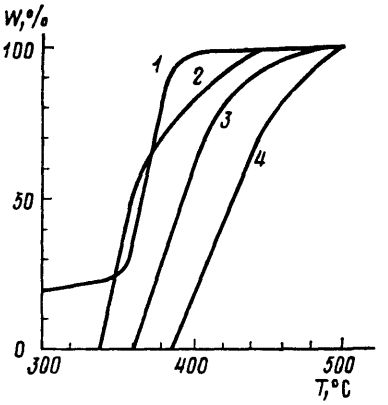

Figure 3. Thermal decomposition of cadmium and tellurium alkyls;[65] W is the ratio of the decomposition rate to the maximum decomposition rate. Compounds: $CdMe_2$ (*1*), $TeEt_2$ (*2*, *3*), $TeMe_2$ (*4*). Pressure of the OMC vapour in the stream of hydrogen: 9 mmHg (*1*), 2 mmHg (*2*, *3*), 10 mmHg (*4*); hydrogen flow velocity: 20 cm s^{-1} (*1*, *3*), 10 cm s^{-1} (*2*), 15.6 cm s^{-1} (*4*).

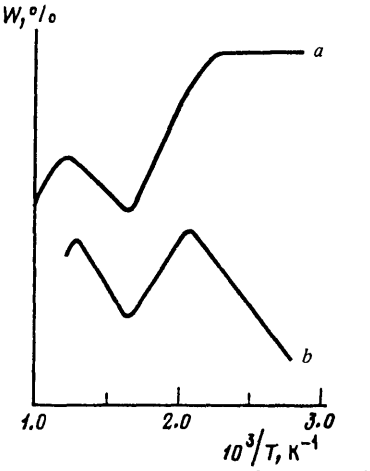

Figure 4. Temperature dependence of the relative rate of growth of cadmium sulphide: *a*) condensation from cadmium and sulphur vapour,[181] *b*) deposition from the vapour of $CdMe_2$ and the decomposition products of dimethyl sulphide.[177]

Up to 1 at.% gallium was detected in layers deposited on gallium arsenide supports; it was assumed[179] that this is transferred to the layer from the opposite side of the support. A mechanism has been proposed[179] for the growth of CdS layers from dimethylcadmium vapour and

hydrogen sulphide. It is suggested that growth takes place by a VLS mechanism with the formation of a two-dimensional liquid from cadmium atoms on the CdS surface. The most perfect layers were obtained with an excess of dimethylcadmium in the stream. Zinc selenide has been obtained by the reaction of DMZ with dimethylselenium in a stream of hydrogen.[180] The plot of the growth rate against the reciprocal of the temperature had a maximum at 560°, and at lower deposition temperatures, W decreased linearly with increase in $1/T$. H_2Se and methane were detected in the gaseous products. The cathodoluminescence spectra of the layers showed an intense band at 600 nm, a number of bands in the range 500–460 nm, and an edge band with phonon structure, indicating that the ZnSe layers obtained had a non-stoichiometric composition and a high density of defects.

The growth rate of a layer of a compound AB by reaction (1) is a function of the pressure in the reactor and the ratio of the fluxes of the OMC and the hydride in the reactor β.[87] Change in the deposition temperature as a result of a difference in the thermal stabilities of the OMC and the hydrides will lead to a change in the ratio β and the pressure in the reactor, and the recording of the temperature dependence of the growth rate may pass through different sections $W(\beta, P)$. For the deposition of ZnSe from the vapour of the OMC and the hydride, the reaction rate over a wide range of conditions is limited by stages II and VII. With increase in temperature and pressure in the reactor, the homogeneous synthesis of ZnSe begins (5 mmHg, 400°), and with decrease in the pressure to 0.5 mmHg, the homogeneous reaction is not observed up to 500°.

The processes of deposition of compounds AB by the reactions of OMC with hydrides have been classified[85] on the basis of the stability of the deposition process and the possibilities for the production of defect-free stoichiometric layers. The $P-T-X$ diagrams for $A^{II}B^{VI}$ compounds were used to construct a hierarchy of pressures: $P_A^{AB(B)}$—the pressure of the vapour of A over a composition with an excess of B, $P_A^{AB(A)}$—the pressure above a composition with an excess of A, and P_A^{cr}—the critical pressure for the formation of nuclei of the substance A on a layer AB with an excess of A. The pressures for the component B, $P_B^{AB(B)}$, P_B^{AB}, and $P_B^{AB(A)}$ are defined similarly. The effective pressures of the atoms P^e are defined in terms of the fluxes of the atoms into the adsorption layer as follows:

$$k_1 P_{OMC} - k_{-1} P_x = (2\pi MkT)^{-1/2} P^e$$

where M is the mass of the OMC molecule or the hydride, and the other quantities were defined above in the examination of the decomposition of the OMC. The pressure P^e and hence the composition of the layer determined by it is measured from the pressure above a layer AB with the stoichiometric composition.

The situations arising during deposition are shown in Table 3. At the temperature T_1 the hydride and the OMC are stable, and the compound AB is deposited by reaction (1); above the temperature T_1, the hydride or OMC decompose. If the sum $P_A^e + P_A^{AB}$ is less than $P_A^{AB(A)}$, the compound AB with a composition in its range of existence will be deposited, but the density of vacancies of the element B increases. If $P_A^e + P_A^{AB}$ is greater than $P_A^{AB(A)}$, a two-dimensional liquid of the element A may be produced on the surface, and if $P_A^e + P_A^{AB(A)} > P_A^{cr}$, condensation of the element A begins. With increase in temperature above T_2, the same regular features will also be observed for the element B, but with allowance for the reaction of the element B with the element A.

Table 3. Relationship between the effective pressures and the composition of AB and the stability of the process.[81]

Temperature	Effective pressures	Composition	Mechanism	Stability
$T<T_1$	$P^e=0$	AB	VC	stable
$T_2>T>T_1$	$P_A^e + P_A^{AB} < P_A^{AB(A)}$	AB, B vacancies	VC	stable
	$P_A^e + P_A^{AB} > P_A^{AB(A)}$	AB(A)	VLS	unstable
	$P_A^e + P_A^{AB} > P_A^{кр}$	*	VLS	stable
$T>T_2$	$P_A^e + P_A^{AB} < P_A^{AB(A)}$	AB	VC	stable
	$P_B^e + P_B^{AB} < P_B^{AB(B)}$	AB	VC	stable
	$P_A^e + P_B^{AB} < P_A^{AB(A)}$	AB(A)	VC + VLS**	unstable
$T>T_2$	$P_B^e + P_A^{AB} > P_B^{AB(B)}$	AB (B)	VC + VLS	unstable

*Formation of inclusions of the element A in the layer is possible.

**Reaction between the atoms of the elements A and B takes place on the surface of the layer.

It should be noted that the growth conditions are unstable when the pressures P_A^{cr} or $P_A^{AB(A)}$ reach the boundary of formation of the two-dimensional condensate.[58] The mechanism of the production of the instability is as follows: on two-dimensional condensation, a liquid phase is produced on the surface; on its surface there is a sharp increase in the coefficients of condensation and reactive adhesion, leading to exhaustion of the starting materials and a change from the VLS to the VC mechanism; subsequently, accumulation of atoms takes place again with a change to the VLS growth mechanism, and the process is repeated. The factor responsible is the hysteresis associated with the condensation–volatilisation process on going from adsorption to the formation of nuclei of the liquid phase or two-dimensional condensates. Fig.2 gives the transverse cross-section of a zinc selenide specimen deposited from the vapour of the OMC and the hydride. In spite of the fact that the growth rate changed by a factor of two along the plane of the specimen (concentration wedge), the frequency of the fluctuations in the composition was constant. This proves that the fluctuations in the selenium concentration in the layer are due to a collective process involving the entire surface. The fluctuations were suppressed by decreasing the pressure in the reactor or by increasing the hydrogen selenide pressure. With decrease in pressure, stoichiometric layers were obtained, and with increase in the hydrogen selenide pressure, layers with an excess of selenium were produced.[85]

In recent years, greatest progress has been made in the preparation of layers of zinc selenide. This is a broad-zone material with lattice parameter close to that of gallium arsenide. ZnSe layers are obtained by the reaction of DMZ or DEZ with hydrogen selenide or dimethylselenium vapour in a stream of a carrier gas or in a vacuum at pressures of 0.1–5 mmHg. Stutius[64,182–186] obtained ZnSe layers by the reaction of the OMC and the hydride at a temperature of 300–350 °C at a reduced pressure of H_2 in

a vertical reactor with a support at an angle of 45° to the axis of flow. He obtained highly perfect layers of zinc selenide on supports of gallium arsenide and germanium, which gave a clearly defined edge band in the photoluminescence spectrum and a ratio $I_e/I_i > 10^3$ (I_i and I_e are the intensities of the impurity and edge photoluminescence).[182] Later papers[64,182] gave the photoluminescence spectra recorded at a lower density of the exciting radiation; the ratio I_e/I_i for films with a thickness of 4 μm was greater than 50, and that for layers with a thickness of 0.1 μm was 0.5. Layers of ZnSe alloyed with aluminium, with a specific resistance reaching 0.05 Ω.cm, have been obtained. The alloys were produced by introducing TMA vapour into the reagent flux.[183,184]

To obtain better matching of the lattice parameters of gallium arsenide and zinc selenide, ZnS_xSe_{1-x} layers with $x = 0.05$ are obtained by adding H_2S to the stream of H_2Se. The decrease in the stresses at the ZnS_xSe_{1-x}–GaAs boundary leads to an increase in the photoluminescence yield of the layer.[183] The dependence of x on the mole fraction of hydrogen sulphide in the stream of hydrogen selenide y was obtained, and an equation relating these parameters was given:

$$x = \frac{0.0159y}{1 - y(1 - 0.0159)} .$$

With change in x in the range 0–0.1, the intensity of the edge band remains constant, and the intensity of the impurity band decreases and has a minimum at $x = 0.05$. This indicates that the intensity of the photoluminescence band at 600 nm is related to the density of defects at the ZnSe–GaAs boundary. To obtain ZnSe (p-type) layers, experiments were carried out to alloy zinc selenide with nitrogen, phosphorus, and arsenic from ammonia, phosphine, and arsine vapour. Nitrogen gives finer levels in ZnSe, but conducting specimens could not be obtained.[64,184]

The deposition of ZnSe from OMC vapour and the hydride at atmospheric pressure of hydrogen has been studied. The dependence of the growth rate on the consumption of the OMC and the hydride, and on temperature, was obtained in the range 450–700°.[187,188] Up to 560°, the value of W is independent of temperature, but above this value it decreases with increase in temperature. With increase in the hydrogen selenide flux, the rate of growth of the layer decreased, and with change in the DEZ flux a maximum in the deposition rate was observed; at a ratio of the DEZ flux to the H_2Se flux greater than 4, growth took place from an adsorption layer enriched in zinc. At a temperature of 520°, inclusions with the composition $Ga_2Se_3.9ZnSe$ were formed at the support boundary.

Zinc selenide has been obtained by the reaction of DEZ with dimethylselenium.[189] The growth rate in the temperature range 350–750° is limited by the transport of the OMC to the support, and the dependence of W on the consumption of the OMC is similar to that discussed above.[187] The preparation of epitaxial layers of ZnSe from a $ZnMe_2$–$SeEt_2$–H_2Se–H_2 mixture (molar ratio 0.45 : 9 : 2.9 : 675) has been reported. Mirror-smooth ZnSe layers with a low level of stresses were obtained.[190] Epitaxial layers of ZnS, ZnSe, and ZnO have been obtained by the reactions of DMZ with the corresponding heterocyclic derivatives of the group VI elements. Single-crystal layers of ZnS and ZnSe were obtained on supports of GaAs,[100] and ZnO layers were obtained on sapphire supports.[191] The chief advantage of the use of heterocyclic derivatives is that it is possible to mix them beforehand with the DMZ vapour.

The possibility of using deposition from OMC vapour to prepare a n-ZnSe–p-GaAs hetero-junction of high quality, suitable for producing electroluminescent and opto-electronic instruments, has been studied.[192–195] Epitaxial layers of ZnSe were obtained by the reaction of DEZ with hydrogen selenide, carried out in a vacuum at temperatures of 300–450° and pressures of 0.1–5 mmHg. Alloys were produced by introducing TMA vapour into the reagent flux. Plates of AGP-1 and AGChTs grade gallium arsenide with a concentration of p-type carriers of 10^{19} cm^{-3} were used as supports. This gave highly perfect ZnSe layers with a structureless edge photoluminescence band and a mirror-smooth surface, with a ratio $I_e/I_i > 10^3$ for a layer thickness of 0.5–5 μm.[188,196] Induced emission was observed on these layers.[197] The resonator was obtained by splitting along the cleavage planes GaAs plates with a deposited ZnSe layer with a thickness of 6 μm, without preliminary treatment of the surface. The threshold density of optical pumping was 50 W cm^{-2} at 77 K. Lasing was also achieved at room temperature.

The specific resistance of the ZnSe (n-type) layers varied in the range 3×10^{-3}–1 Ω.cm with change in the concentration of n-type carriers in the range 2×10^{18}–10^{16} cm^{-3}. For the production of devices, it is necessary to obtain a perfect n-ZnSe–p-GaAs hetero-junction with a low resistance. Examination of the reactions at the ZnSe–GaAs boundary showed that the interaction of gaseous hydrogen selenide with the p-GaAs surface can lead to displacement of the p–n transition in gallium arsenide, the formation of an insulating layer at the boundary, and the production of structures of the type n–p–n–p; this has been confirmed experimentally.[193]

The intermediate layer at the ZnSe–GaAs boundary has been studied by photoluminescence methods. The spectra recorded at right angles to the surface of the specimen contained an impurity photoluminescence peak at 600 nm. Observation of the photoluminescence from the splitting showed that the emission at 600 nm is localised in a range of 0.1–0.2 μm adjoining the gallium arsenide surface. Since the exciting radiation is completely absorbed in zinc selenide at a thickness of less than 0.1 μm, the observation of the band at 600 nm in the photoluminescence spectrum indicates that it is excited as a result of ambipolar diffusion of the carriers. Comparison of the intensity of the impurity photoluminescence band from sections of the ZnSe layer with different thicknesses made it possible to measure the diffusion length in zinc selenide specimens, which amounted to 2.5 μm at 300 K and more than 6 μm at 77 K.[192] The formation of the intermediate layer is related to the catalytic decomposition of hydrogen selenide on the gallium arsenide surface. Thus when gaseous H_2Se is supplied to the reactor, drops of selenium decorate the GaAs surface at 300°.[196] In the deposition of ZnSe on GaAs, two sets of conditions are realised in succession; the first corresponds to hetero-epitaxy, with the catalytic decomposition of hydrogen selenide and the growth of a ZnSe layer with an excess of selenium, and the second corresponds to auto-epitaxy, with the growth of stoichiometric zinc selenide.

In Ref.198, deposition from OMC vapour and the hydride in a vacuum gave zinc selenide layers with a thickness of 0.03–0.1 μm, whose photoluminescence spectrum, in contrast to Ref.64, gave a ratio $I_e/I_i \cong 10$, indicating the absence of an intermediate layer at the ZnSe–GaAs boundary. The photoelectric properties of hetero-junctions have been studied for ZnSe specimens alloyed with aluminium to a level of 10^{16}–3×10^{-18} cm^{-3}. The carrier collection coefficient increased with increase in the concentration of carriers; relative to the number of photons reaching the

p–n junction, it amounted to 0.92–1.00 in the range 460–890 nm, and at wavelengths less than 460 nm it varied in the range 0.2–0.3; this indicates the long length of ambipolar diffusion in the epitaxial layers (Fig.5).

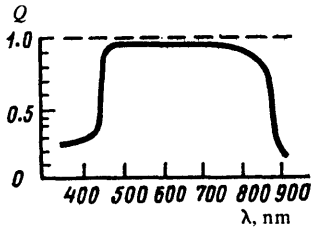

Figure 5. Dependence of the quantum efficiency Q of the hetero-junction p-GaAs–n-ZnSe on the wavelength of light.[198]

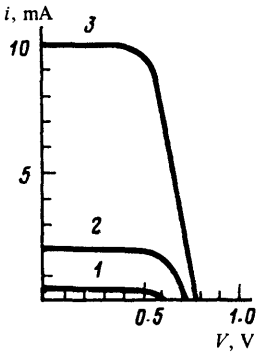

Figure 6. Load characteristics of a diode based on ZnSe–GaAs for different solar radiation powers: 0.4 MW cm^{-2} (*1*), 180 MW cm^{-2} (*2*), and 900 MW cm^{-2} (*3*).[198]

The forward and reverse branches of the voltage-current characteristic are approximated by the expressions:

$$i = i_0 \exp\left(\frac{V}{1.7\,kT}\right), \quad i = i_1 \exp\left[-C(V_0 - V)^{-\frac{1}{2}}\right]$$

where $i_0 = 10^{-8}$–10^{-9} A cm^{-2}, $C = 13$–14, and $V_0 = 1.30$–1.35 V. These forms of the forward and reverse branches of the voltage-current characteristic indicate that the predominant mechanism of current flow in the given diode is by tunneling.[199] The recording of the C–V characteristics of the hetero-junction showed that close to the ZnSe–GaAs interface there exists a layer of thickness 50 nm, which has a low concentration of carriers and which becomes narrower with increase in the concentration of carriers. The load characteristics of the diode were recorded using specimens with dimensions of 3 × 2 mm^2 without a brightening coating under direct solar radiation AM2 (Fig.6). The diode current was limited by the resistance of the contact, and not by the resistance of spreading; the efficiency of the diode varied in the range 15–18%, depending on the power of the incident radiation; the efficiency calculated with allowance for the production of a brightening coating was 18–22%.[198]

Experiments have been carried out to obtain zinc selenide from OMC vapour and the hydride at low carrier gas pressures. Conducting layers of zinc selenide were obtained without alloying at a deposition temperature of 250–300°; the conductivity decreased with increase in the deposition temperature to 370°, indicating uncontrolled alloying of the layers at low deposition temperatures.[200–202]

A number of studies have been devoted to the preparation of mercury telluride and the ternary system $Hg_xCd_{1-x}Te$.[203–206] The main difficulty in the production of this system is the high vapour pressure of mercury over compositions rich in mercury, which restricts the upper temperature of deposition to 400–420° and requires rapid cooling of the support with the epitaxial layer obtained when the deposition is complete. The deposition is carried out using a mixture of Hg–$CdMe_2$–$TeMe_2$–H_2 vapour, transported by a stream of hydrogen into the deposition zone. CdTe plates oriented with the (100), (110), or (111) faces are used as supports; the deposition temperature is 350–410°. An intermediate layer with a thickness of 0.4 μm, due to the diffusion of mercury in the support, was formed at the film–CdTe boundary. Increase in x was accompanied by a sharp change in the morphology of the surface of the layers; at $x < 0.2$, the surface was formed of irregular steps with cracks of a depth of up to 10 μm; at $x > 0.2$, the surface became mirror-smooth. Layers with an excess of tellurium showed n-type conductivity, and those with an excess of mercury showed p-type conductivity. The conductivity of the layers was determined by the consumption of mercury vapour in the reactor; the rate of deposition increased with increase in temperature.

A relatively small number of studies have been devoted to the preparation of epitaxial layers of $A^{IV}B^{VI}$ compounds. The deposition is carried out using the reaction of alkyls of group IV elements with hydrogen sulphide, hydrogen selenide, or tellurium alkyls in a stream of carrier gas (hydrogen). The temperature of deposition of the epitaxial layers was 550° for SnS, 500° for SnSe, 625° for SnTe, 550° for PbS and PbSe, 500° for PbTe, and 550–625° for $Pb_{1-x}Sn_xTe$.[52]

Table 4. Organobimetallic compounds used to prepare $A^{IV}B^{VI}$ compounds.[70–72]

Compound	T, °C	Solid products	Gaseous products
$(RS)_4Si$	500—600	SiS_2	SR_2
$(CH_3S)_2Cd$	400	CdS	SMe_2
$(R_3Ge)_2Hg$	400	Ge	C_1—C_4 (gas)
$Et_3SiTeGeEt_3$	450	GeTe	$TeEt_2$, *EtH*
$(Et_3Ge)_2Te$	450	GeTe	$GeEt_4$, $TeEt_2$
$(Et_3Ge)_2S$	450	GeS	$GeEt_4$
$Et_3GeTeEt$	450	GeTe	$GeEt_4$, $TeEt_2$
$(Et_3Sn)_2S$	350	SnS	$SnEt_4$
$(Et_3Sn)_2Te$	300	SnTe	$SnEt_4$, $SnEt_3H$
$Et_3SnTeEt$	400	SnTe	$TeEt_2$, $SnEt_4$

At lower temperatures, the compounds $A^{IV}B^{VI}$ can be obtained by the thermal decomposition of organobimetallic compounds containing a metal–chalcogen bond;[70–72] the deposition of the binary compound is identical to the deposition of the simple compound, for example of silicon or germanium. The process is simplified considerably, since the stage involving the mixing of the components is eliminated, making it possible to stabilise the stoichiometric

composition of the layer over the entire area of the support. Data on the preparation of epitaxial layers of compounds $A^{IV}B^{VI}$ from the vapour of organobimetallic compounds are given in Table 4. It can be seen from Table 4 that the deposition temperature of the layers is lower than that when a mixture of OMC vapour and the hydride is used.

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Thus deposition from OMC vapour is widely used to produce micro- and opto-electronic devices with exceptional parameters. New methods for the deposition of epitaxial layers are being rapidly developed and introduced into practice, the range of OMC used in technology is being expanded, and the search for new compounds is being continued. In addition, the theory of the deposition of epitaxial layers of binary compounds is being slowly developed (for 150–200 technical papers there is fewer than one paper on the study of the mechanism of the process), and this is holding up the introduction of methods for the deposition of epitaxial layers from OMC vapour in industry.

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Spectroscopic Study of the Steric Effects in Organic Compounds of Silicon Subgroup Elements

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The principal theoretical and experimental approaches to the study of the influence of the steric effects of substituents on the properties of organic and organoelemental compounds are examined. The role of these effects in complex formation with participation of organic compounds of silicon subgroup elements and the influence of steric effects on the conjugation in these compounds are analysed.
The bibliography includes 238 references.

CONTENTS

I. Introduction 786
II. General ideas concerning steric effects 788
III. Experimental studies of the steric effects in compounds of silicon subgroup elements 790

I. INTRODUCTION

The idea of a significant role of steric effects in chemistry, apparently put forward for the first time by Mayer,[1] has now undergone an extensive development not only in stereochemistry[2,3] but also in all other branches of chemistry.[4-10] Thus in the study of reactivity the possibility of the approach of the reacting molecules in space is considered to be an important factor determining the barrier to the reaction, i.e. the activation energy.[11,12]

The role of steric effects does not reduce solely to the alteration of the reactivity of the compound by regulating the degree of shielding of the reaction centre on varying the bulk of the substituents adjoining the centre. Another factor is the steric inhibition of resonance, i.e. partial or complete breakdown of the conjugation in the molecule (and hence also a change in its reactivity) after the introduction of bulky substituents into the molecule. Such substituents prevent the steric disposition of atomic fragments necessary for their conjugation with one another. Both the first[2,3,4,7,13,14] and second[15,16] factors have been examined in fair detail for organic compounds. For organoelemental compounds, the existing factual data are not so extensive and have been surveyed to a lesser extent, although there are reviews on the chemistry of phosphorus[17,18] and silicon[19-22] derivatives. At the same time, in organoelemental chemistry steric effects play a more varied role compared with carbon compounds. We shall differentiate three aspects of the influence of steric effects: on the reactivity, on the complex-forming capacity, and on conjugation in organoelemental compounds.

1. The Influence of Steric Effects on Reactivity

Organoelemental and particularly organopolyelemental compounds, containing chains of heteroatoms, possess polar and highly polarisable chemical bonds. Although such compounds are entirely stable thermodynamically, they are distinguished by an enhanced (compared with organic compounds) reactivity. The reactivity of organoelemental compounds varies within very wide limits not only under the influence of the inductive and resonance effects but also (sometimes predominantly) owing to the steric blocking of the reaction centres by bulky substituents. In the literature, including the review literature[6,8,10,19,20,22,23] there exist numerous clear examples of the inter-relation between the reactivity of organoelemental compounds and the steric effects of the substituents. The present review presents only isolated data concerning the influence of steric effects on reactivity and deals particularly with studies designed specifically to reduce the reactivity of organoelemental compounds.

For example, the thermal stability of the compounds $(R_3Sn)_2Hg$ increases significantly on passing from lower alkyl to phenyl substituents and to an even greater extent the trimethylsilylmethyl[24] substituent, which exhibits pronounced steric effects. Similarly, when CH_3 is replaced by C_6H_5 and C_6F_5 in the compounds $(R_3Ge)_2Hg$, which is accompanied by an increased shielding of the mercury atom, their reactivity diminishes and their thermal stability increases.[25] A sharp increase in thermal stability occurs on passing from $[(C_6H_5)_3.Ge]_2M$ (M = Hg or Cd) to $(C_6H_5)_3Ge-M[Ge(C_6H_5)_3]Ni(\eta^5-C_5H_5)-M-[Ge(C_6H_5)_3]Ni(\eta^5-C_5H_5)-M-Ge(C_6H_5)_3$, in which the atoms M are fully shielded by the ligands.[25,26] Yet another example of the influence of steric effects, this time not on the reactivity but on the very possibility of the existence of compounds, is provided by the synthesis of the derivatives $Mes_2Si=SiMes_2$, where Mes = mesityl,[27,28] and $[(CH_3)_3Si=C[OSi(CH_3)_3]R$, where R = $CAlk_3$ or 1-adamantyl,[29,30] with double bonds at the silicon atom. Despite the lack of theoretical prohibition of their existence, compounds of this type had not been isolated under normal conditions as stable species until the investigations of West and Fink[27,28] and Brook and co-workers,[29,30] and were merely detected in low-temperature matrices by means of physical methods or their formation was assumed as intermediates in reactions (see, for example, Gusel'nikov and Nametkin[31]). There is no doubt that, together with the electronic effects of substituents, the steric effects of bulky mesityl, adamantyl, t-butyl, and other substituents are important for the stabilisation of the double bond at the silicon atom.

2. The Influence of Steric Effects on the Complex-Forming Capacity

On passing from organic to organoelemental compounds, the possibilities for the formation of complexes of the donor-acceptor type (DA complexes) is greatly enhanced. Whereas the carbon derivatives R_3C-X (X is an unsaturated group of the type of aryl, alkenyl, naphthyl, etc.) are formed predominantly in complexes with electron acceptors by virtue of the electron-donating properties of the fragments X,[32,33]

two further types of DA complexes are extremely characteristic of organoelemental compounds.[34-37] These are complexes with an increased coordination number of the central element as well as DA complexes in which element–carbon bonds with low ionisation potentials play the role of carriers of the electron-donating properties.

Analysis of the characteristic features of the formation of these three types of DA complexes has shown that in many cases the steric effects play a major role in complex formation. In the general case the steric accessibility of the atom E in organoelemental compounds of the type R_nE (R is an alkyl group or a carbo-functional substituent and n is the oxidation state of the central element E) is determined not only by the size of R but also by the size of E and the length of the E–R bond, i.e. by the distance from the bulky group R to the reaction centre E. Similarly, when an organoelemental compound $R_{n-1}E-C\diagup\!\!\diagdown$ participates as an electron donor, by virtue of the fragment $E-C\diagup\!\!\diagdown$, in complex formation with an acceptor, then in this instance one must take into account both the dimensions of the given fragment and the steric effects of the substituents R and the atom E in the formation of the DA complex. Finally, in compounds of the silicon subgroup elements R_3C-X for $n = 4$, the steric effects of the R_3E and R_3C substituents apparently do not influence the formation of the DA complexes between the unsaturated groups X and the acceptor molecules (tetracyanoethylene, iodine, etc.).[38,39]

For compounds with several bulky organoelemental substituents at the unsaturated group X (for example, in the benzene ring or at the double bond), the influence of the steric effects of the substituents becomes comparable or even greater than their inductive and resonance influences.[40-42] A characteristic feature of DA complexes, which follows both from a theoretical study by quantum-chemical methods and from experimental data (see the relevant reviews[13,32-34]), is the mutual approach of the donor and acceptor centres of the interacting molecules in the complex to a distance optimal for the DA interaction, which depends on the nature of the given centres. The introduction of bulky substituents into the molecules constituting the DA complex can prevent such approach for purely steric reasons. This steric "inhibition" of the DA interaction is reflected in the spectroscopic and thermodynamic characteristics of the complex.[10,43]

It must be emphasised that the steric effect of substituents in the donor or acceptor molecules in complex formation are to some extent conventional in character. Indeed, with increase of the steric accessibility of the interacting centre in the donor (acceptor) molecule, the steric hindrance to the formation of a DA complex with the acceptor (donor) molecule diminishes even if the latter contains several bulky substituents.

As an example, one may quote the stannylacetylenes $(CH_3)_{3-n}R_nSnC\equiv CR$ with bulky substituents R (t-butyl, etc.), which can hinder the formation of DA complexes via the triple bond.[44] Steric effects are distinctly manifested in the formation of complexes with molecular iodine and become enhanced when the groups R accumulate in the molecule. In contrast to this, the substituents R do not in any way hinder the formation of a hydrogen bond with phenol, i.e. in DA complexes of this type stannylacetylenes do not exhibit the features of sterically hindered systems. The above example emphasises the difficulty of interpreting the experimental data in order to elucidate the characteristics of the influence of steric effects, since the latter are manifested in many instances as a property not of the donor acceptor separately but of the DA complex as a whole.

Generally speaking steric hindrance to the formation of complexes is pre-determined by the structure of the initial donor and acceptor molecules. For this reason, even if the donor (acceptor) centre is sterically blocked by bulky substituents and the acceptor (donor) centre is distinguished by a considerable steric accessibility, then the properties of the DA complex as a whole may be the same as in a system where there is no steric hindrance to complex formation.

Another factor closely related to the complication of the interpretation of steric effects already examined is the possibility of a change in the donor or acceptor properties of the initial components of the DA complexes owing to the steric effects of the variable substituents in their molecules. It is known, especially in organic chemistry,[2,4,7,13,15,45] that the introduction of bulky substituents can entail a weakening of the electronic intermolecular interactions in the molecules of the other species constituting the complex. If the donor or acceptor centre of a component of the DA complex is involved, then, together with the steric hindrance to the mutual approach of the centres, there is a possibility of secondary complications, which exert their influence via the steric effects in the initial components and the donor–acceptor properties of such interacting centres. From the above brief list of the complications introduced by steric effects into the complex-formation process, it already follows that the study of these effects in organoelemental compounds constitutes as a whole an extremely large and varied problem. It is useful to examine initially the influence of steric effects for a narrower range of model systems. There are organic compounds of silicon subgroup elements which have served for a long time as models for the solution of the most important problems in organoelemental chemistry.[42,46,47] The important role of steric effects and conjugation effects in organoelemental chemistry has been demonstrated in the literature in relation to these systems.

3. The Influence of Steric Effects in Conjugation

The problem of the inter-relation of the steric and resonance effects in organoelemental compounds is of independent importance. Indeed, conjugation effects in organoelemental chemistry are distinguished by a greater variety than in the chemistry of carbon. Together with the resonance effects characteristic of organic compounds, the role of hyperconjugation (σ,π-, σ,σ-, and σ,p-conjugation) is sharply enhanced in organoelemental compounds[42] and a conjugation effect arises which is in principle impossible for carbon compounds, namely the so-called $(p-d)\pi$ interaction which is traditionally attributed to the presence of unoccupied *nd* orbitals in the central elements E.[46,47]

It was shown a comparatively long time ago[48,49] and has been subsequently frequently confirmed by means of various methods, including spectroscopic methods (in particular for compounds of the silicon subgroup elements[42,46]), that there is a profound analogy between various conjugation effects. Therefore the magnitude of the effect both in the resonance interactions of the type of π,π- and p,π-conjugation, which are common in organic chemistry, and in the hyper-conjugation effects, which are more specific to organoelemental compounds, depends on the steric disposition of the interacting orbitals.[42] For example, the degree of the σ,π-conjugation (the variety of hyperconjugation which has been most thoroughly investigated) can be regulated within wide limits by varying the stereoelectronic state of the molecule.[23,42,50,51] The presence or absence of a strong resonance effect of the σ,π-conjugation, comparable in magnitude to that of the typical p,π-conjugation in organic compounds, in many instances alters radically the reactivity.[48,49,52]

Without analysing the role of steric effects, it is impossible to study the characteristics of another resonance effect specific to organoelemental compounds of Group IVB elements, namely that of the $(p-d)\pi$ interaction. The steric effects in such interactions are examined in greater detail below. Here we shall mention that the $(p-d)\pi$ interaction is less sensitive to steric effects, by virtue of the characteristic features of the geometry of the *d* orbitals,[47,53,54] than the σ,π-conjugation. Nevertheless, when there are several substituents X (with unshared *p*-electron pairs) at the central atom E (with unoccupied *nd* orbitals), the overall effect of the $(p-d)\pi$ interaction in the molecule due to pure steric effects, which specify the conditions governing the overlap of the interacting p_π and d_π orbitals, is significantly smaller than might have been expected on the assumption that the contributions by each E–X bond are additive.[47,53-55]

Thus there is a close inter-relation between the steric structure of organoelemental compounds, the steric effects of the substituents in their molecules, and the resonance intramolecular interactions. Determination of the characteristic features of this interaction for model compounds of silicon subgroup elements is the second aim of the present review.

Extensive data obtained in studies of the dependence of both the capacity for complex formation of organic compounds of silicon subgroup elements and the conjugation effects in these compounds on steric effects have accumulated in the literature. Despite this, both aims of the review are of current importance, since the available data have been subjected to an inadequate systematic treatment and conclusions reached in many studies are frequently ambiguous and their evidential value is low. The important question of the reliability of given studies devoted to the analysis of the extent to which the electron-donating properties of organic compounds of Group IVB elements are weakened owing to the steric effects of the substituents is fairly complex. Particular attention was therefore devoted in this review to the elucidation of the validity and soundness of the literature data.

II. GENERAL IDEAS CONCERNING STERIC EFFECTS

The aim of this Section of the review is to formulate the general ideas concerning the steric effects of substituents which follow from the existing reviews[3-5,7,8,13,15-17,43,56-59] and other publications of fundamental importance.

It has been emphasised[7] that one of the key postulates is that the set of phenomena combined by the term "steric effects of substituents" must be regarded as a special case of a more general problem, which is the object of conformational analysis.[60] A quantitative theoretical approach to the study of steric effects must therefore be based on the advances in the theory of conformational analysis, i.e. on quantum-chemical calculations of the total energy of the molecule as a function of the angles of rotation, which makes it possible to establish the most stable conformation.

Conformational analysis has led to the accumulation and systematic treatment of experimental data for the potential barriers to internal rotation and for the differences between the free energies of the conformers. Historical surveys of these studies have been published[16,56,58] and reviews of modern data for several thousands of compounds also exist.[3,16,58,59] In many cases the relations between the barriers to rotation and the electronic and steric effects are manifested extremely clearly. Thus the barriers to internal rotation in ethane derivatives (3–20 kcal mol^{-1}) are higher than for ethane itself (3 kcal mol^{-1}) and exhibit a tendency to increase with increase in the bulk of the substituents at the carbon atom.

The spatial removal to a greater distance of the groups involved in free rotation with increase in the length of the chemical bond connecting them lowers the barrier to internal rotation, which follows, for example, from a comparison of the barriers for Cl_3CCCl_3, Cl_3CSiCl_3, and $Cl_3SiSiCl_3$ (respectively ~11, 4.5, and ~1 kcal mol^{-1}); this is also indicated by the fact that the free energy of activation for internal rotation is significantly smaller in $[(CH_3)_3C]_2HSiSiH[C(CH_3)_3]_2$ (13.7 kcal mol^{-1} [61]) than in $[(CH_3)_3C]_2HCCH[C(CH_3)_3]_2$ (23 kcal mol^{-1} [62]) and also by the ratio of the molecular dipole moments of ethane and disilane derivatives.[63]

In compounds of Group IVB elements the type of $E(CH_3)_4$ an increase in the bulk of the atom E in the sequence C, Si, Ge, Sn lowers the barrier to internal rotation from ~4.5 to 2, 1.5, and <1 kcal mol^{-1} respectively.[61]

Important data have been obtained in the study of the barriers to internal rotation in benzene derivatives. The barrier to the internal rotation of the methyl group in toluene, which is almost zero, increases significantly on passing to $C_6H_5SiH_3$, which indicates an increase in the multiplicity of the silicon–phenyl bond due to the $(p-d)\pi$ interaction.[64] In the Ar–X–Ar (X = O, CO, etc.) systems and also in *ortho*-disubstituted biphenyls, structures with the "propeller" rotation of the aromatic rings are produced for steric reasons despite the fact that a planar molecule would have been most favourable for conjugation. It is striking that, with increase in the size of the *ortho*-substituents in halogeno-biphenyls, the dihedral angle steadily increases.

The review literature (see, for example, Refs.3, 16, 58, and 59) presents compilations of data for barriers to internal rotation also in other types of organic compounds. For example, it has been established for esters $R-C(=O)-OR'$ that the difference between the energies of the *cis*- and *trans*-isomers, arising as a result of rotation about the C–O bond, increases with increasing size of the substituents R and R'. At the same time, it follows from literature data that it is frequently impossible to observe a very clear and evident relation between the potential barriers to internal rotation and the conformer energy difference, on the one hand, and the characteristics of the molecular structure and especially the steric influence of the substituents, on the other. Together with experimental studies, computational empirical as well as semiempirical and non-empirical quantum-chemical methods are being developed in conformational analysis.

In the empirical methods the molecule is regarded as a system of interacting atoms.[58] Here five different contributions to the potential energy of the molecule, taking into account the energy of the non-bonding interactions between the atoms as well as the influence of the deformations of the angles and bonds and the electrostatic contribution to such interactions, are distinguished. Although the empirical methods do in fact make it possible to obtain practically important estimates of the potential barriers to internal rotation without resorting to extremely complex calculations, they do not provide a clear understanding of the nature of the barrier.[65]

An improved reliability of the calculations of the barriers to rotation and of the energy differences between the conformers can be achieved by employing semiempirical quantum-mechanical methods. The possibilities of the semi empirical methods have been assessed in two investigations.[58,65] It was found that, despite the importance of the information obtained (for example, for the estimation of the barriers to rotation in a series of compounds with related structures), these methods have limited applicability, because they include a series of empirically determined parameters. The dependence of the result on the suitability of the selected parameters lowers the

objectivity of the semiempirical methods. Non-empirical *ab initio* quantum-chemical methods have therefore been developed to an increasing extent recently for calculations of the potential barriers to internal rotation and of the total energy of the molecule as a function of the angles of rotation.[65] The theoretical principles of conformational analysis should apparently be developed in the course of systematic studies of the principle classes of compounds by non-empirical methods. However, so far this problem is extremely far from solution, in particular because of the high cost of such calculations even for molecules of medium size, the inadequate effectiveness of the computer programmes, and the necessity to employ faster computers for calculations on fairly complex molecules.[65] The application of *ab initio* methods has not so far led to a complete understanding of the nature of the barriers to internal rotation, but it has been shown in many instances that, for the most stable conformation of the molecule, the bond around which internal rotation takes place is characterised by the highest electron density, i.e. exhibits the maximum stability.[65–67]

We shall consider certain calculated quantum-chemical data for organosilicon molecules. Non-empirical calculations carried out in terms of different basis sets, established a significantly lower barrier to inversion at the nitrogen atom in the H_3SiNH_2 molecule than in the ammonia molecule and an increased multiplicity of the silicon–nitrogen bond due to the $(p-d)\pi$ interaction;[68] they confirmed the covalent character of the silicon–oxygen bond under conditions where the Si–O–Si angle in the disiloxane fragment is varied within wide limits;[69] they revealed a preference for a non-planar structure in 5-silylcyclopentadiene (apparently as a consequence of hyperconjugation), in contrast to its carbon analogue.[70]

Semi-empirical calculations have been used more widely for organosilicon compounds in conjunction with several variants of the zero differential overlap—the CNDO and INDO methods. As already mentioned above, the quality of the semiempirical calculations depends on the soundness (or success) of the selection of the computational parameters. A typical example is provided by the attempts to reproduce by the calculations the experimentally established planar structure of trisilylamine $(H_3Si)_3N$. According to Sadimenko et al.,[69] agreement between calculation and experiment has been achieved in only one[71] of the several variants of the calculation. The barrier to rotation in trisilylamine obtained from the calculated data of Rank et al.[72] is too high. The necessity for a critical approach to the results of semiempirical calculations follows, in particular, from the fact that one of the most important features of organosilicon compounds, namely the degree of their $(p-d)\pi$ interaction (for example, in the silicon–nitrogen bond) depends on the molecular geometry.[71,73] Inaccurate information about the geometry obtained from the calculations can therefore lead to incorrect conclusions about the importance of such interaction.

It follows from semiempirical calculations that a change in the conformation of the $H_3SiOSiH_3$ molecule, accompanied by the variation of the Si–O–Si angle, induces not only a change in the energy of the highest occupied molecular orbital but also the inversion of the sequence of orbitals.[74]

It has been established by the CNDO/2 method that the non-bonding Hal...Hal interactions are sharply weakened on passing from CF_4 to CCl_4 and their silicon analogues[75] and also to other fluoro- and chloro-silanes.[76,77] For the more complex molecules of methylsilanes and fluoromethylsilanes, semiempirical calculations[78–80] yield conformations which agree with experiment, but they are relatively unsuitable for the estimation of their barriers to rotation.

A wide variety of the conformations of the polysilanes Si_nH_{2n+2}, which has been confirmed indirectly by experiment, follows from calculations by the CNDO method.[81] The calculations also indicate an explicit preference for the geometry of benzyltrimethylsilane which is most favourable for hyperconjugation.[82] According to the calculated data of Drews et al.,[83] the minimum in the total energy of the trimethylsilylaniline molecule is attained for the geometry in which one methyl group is located in the plane of the aromatic ring.

Thus, while taking into account the above remarks about the applicability and accuracy of the quantum-chemical methods, one should note their important role in the establishment of the theory of conformational analysis, i.e. ultimately also in the solution of the problem of the influence of steric effects on chemical properties. At the same time, the limited amount of literature data precludes at present sufficiently unambiguous conclusions concerning the role of steric effects in organic chemistry; the data obtained for organoelemental compounds are clearly insufficient.

Together with the methods for the investigation of the role of steric effects examined above, a completely different approach proposed by Ingold and Taft,[7,9,14] has developed independently. It is based on the assumption (supported subsequently by theoretical considerations[7]) that it is possible to represent the Gibbs free energy ΔG of reaction or activation by the sum of independent components, i.e. $\Delta G = \Delta G_I + \Delta G_R + \Delta G_S$, which reflects the influence of the inductive (I), resonance (R), and steric (S) effects. This linear free energy principle holds for enormous numbers of chemical processes (and also in the correlation of many physical properties[84]) and among them it is possible to select those in which the influence of one of the effects on ΔG predominates. The process in which the steric effects exert a dominant influence ($\Delta G = \Delta G_S$) is in particular the acid hydrolysis of the esters XCH_2COOR. The logarithms of the hydrolysis rate constants, which are proportional to ΔG, depend on the steric constants E_S of the variable substituents X:[14]

$$\lg\left(\frac{k}{k_0}\right) = \delta E_S ,$$

where k and k_0 are respectively the rate constants for the acid hydrolysis of the substituted (XCH_2COOR) and unsubstituted (CH_3COOR) esters and δ is a constant which depends on the type of reaction series (the nature of R). Assuming that for hydrogen $E_S = 0$, the steric parameters E_S for a large number of substituents have been obtained.[14,84] Although theoretical evidence supporting the view that the constants E_S characterise only the steric effect has been presented in the literature,[85] the initial fundamental publication[14] was followed by a series of studies whose authors analysed, on the one hand, the possibility of the presence of a hyperconjugation component in E_S[7,45,86,87] and, on the other hand, examined the physical significance of E_S and estimated the validity of the experimental methods for each determination.[45,88,89] Ultimately no unambiguous conclusions were reached concerning the role of hyperconjugation, whose contribution to E_S depends on the type of compounds investigated[45] and in many instances is apparently extremely low.[87]

Analysis of the most thoroughly determined values of E_S (for 107 substituents) has shown[45] that the E_S for simple symmetrical

groups X are linearly related to the quantity $\nu_x = r_X - r_H$ [89] which represents the differences between the van der Waals radii of the atom X and the hydrogen atom. However, for bulky asymmetric groups and a complex steric configuration of the type of CR'R"R"' with different substituents, there is no simple correlation between the experimental E_S and the ν_x. The quantity ν_x for such groups may not have just one value but at least two, the minimum and maximum values,[88] and in neither case is a correspondence observed[45] between the calculated and experimental E_S. Even greater difficulties arise on passing from aliphatic to aromatic compounds, in which the *ortho*-effect of the substituents cannot be explained[90] solely by steric factors. Thus it has not been possible to use the parameter E_S to characterise the steric effects in cyclohexane derivatives.[91]

On passing to organoelemental compounds, the non-universality of the parameter E_S, which characterises in general (taking into account the above remarks concerning very complex substituents) the size of the substituent, becomes still more evident. Indeed, in these compounds it is necessary to take into account in the first place no longer simply the size of the substituent, i.e. the parameter ν_x or E_S (although even they are unknown for many organoelemental substituents), but the distance of the substituent from the reaction centre. Furthermore, the distance between a bulky substituent and the reaction centre can vary within wide limits both owing to the changes in the length of the chemical bond between them when the central element is varied and as a consequence of the possible mutual approach in space of the substituent and the reaction centre even when they are separated by several bonds. The size of the substituent alone does not then generally determine the steric situation and it can be characterised by the parameters of the type E_S and ν_x only in exceptional cases.

Two methods have been proposed for the estimation of steric effects in similar complex instances. In the method of cone angles,[17,92] developed in relation to compounds of the type of $Ni(PR_3)_4$, account is taken of the change in the size of the bulky ligand PR_3 as a function of the type of R. This change is characterised by the angle in the plane and the distance from PR_3 to the reaction centre (the nickel atom) is assumed to be unchanged. In the more sophisticated method of solid angles,[25,26,93] the steric shielding of the central element E in ER_n is estimated in terms of the sum of n solid angles (with the vertex at the atom E) occupied by the substituents R. The method of solid angles can also be used to estimate the shielding of atomic fragments, for example by an individual chemical bond or the remainder of the molecule.[25,26,93] This method has been used, in particular, to estimate the steric accessibility of a donor centre localised predominantly at a tungsten atom with formation of molecular complexes with derivatives of dicyclopentadienyltungsten dihalides.[94] A steric model, close in its physical significance to the method of solid angles, has been proposed by Galkin and Cherkasov.[95]

Thus it is impossible to propose a set of universal constants characterising steric effects. Among the methods for the estimation of the role of steric effects in the molecule and especially in a series of compounds with consistently varied substituents, that of solid angles appears to be the most promising. Its use, however, requires the application of computers and data (sometimes exact) for the molecular geometry.

As a problem in physical organoelemental chemistry, that of steric effects can be formulated by isolating from the overall Gibbs free energy the component due to the influence of steric factors. Despite the limitations and difficulties arising under these conditions, this approach is in fact used in most investigations.

III. EXPERIMENTAL STUDIES OF THE STERIC EFFECTS IN COMPOUNDS OF SILICON SUBGROUP ELEMENTS

1. Steric Effects in Complex Formation

The data presented in this Section are classified in terms of the fragments E–X (E is a silicon subgroup element and X is a substituent).

(a) Compounds with E–Group V Element Fragments

Steric effects have a marked influence on the properties of the carbon analogues of these compounds, namely amines.[2,5,13,58] For example, tertiary alkylamines have an anomalously low basicity due to the steric effects of the substituents at the nitrogen atom.[96] A linear relation between the inductive constants σ^* of the substituents and the basicity has been observed for primary, secondary, and tertiary amines.[96] The points corresponding to compounds with bulky substituents show consistent deviations from these straight lines. Another characteristic example is that of the sharp increase of the basicity of aromatic amines with increasing bulk of two alkyl groups at the nigrogen atom. The basicity of the nitrogen atom increases owing to the steric inhibition of the p,π conjugation between the aromatic π-system and the substituent NR_2, which does not occupy the position most favourable for conjugation, since this position is prohibited owing to the intimate steric contacts between R and the *ortho*-hydrogen atoms of the aromatic ring.[97]

Steric effects exert a significant influence also on the properties of compounds with a silicon–nitrogen bond. Its length (1.71–1.76 Å)[98] is less than the sum (1.80 Å) of the covalent radii of the silicon and nitrogen atoms corrected for the amount of ionic character of the bond.[99] The shortening of the Si–N bond can be attributed to the influence of the $(p-d)\pi$ interaction,[46] which increases the multiplicity of this bond. However, steric factors also make a definite contribution, which follows from the increase of the length of the silicon–nitrogen bond when the methyl group is replaced by the bulkier silyl group in the series (the Si–N bond lengths are given in brackets in Å) $N(CH_3)_2SiH_3$ (1.715), $N(CH_3).(SiH_3)_2$ (1.726), and $N(SiH_3)_3$ (1.734), on replacement of the silyl group by the trimethylsilyl group in the series $NH(SiH_3)_2$ (1.725), $NH[Si(CH_3)_3]_2$ (1.738), $N(SiH_3)_3$ (1.734), and $N[Si(CH_3)_3]_3$ (1.760), and on replacement of a hydrogen atom in the organoelemental substituent X on passing from $NH[Si(CH_3)_3]_2$ to $NX[Si(CH_3)_3]_2$.[98] At the same time the barrier to the internal rotation of the SiH_3 groups in $N(CH_3).(SiH_3)_2$ (3.3 kcal mol^{-1}) is higher than in $N(CH_3)_2SiH_3$ (1.5 kcal mol^{-1}), which is believed[100] to demonstrate (together with steric factors) a greater contribution of the $(p-d)\pi$ interaction to the Si–N bond in the first of these compounds. The steric effects of the bulky trimethylsilyl groups leads to the appearance of a fairly high barrier to the rotation about the N–N bond in the radical-cation $[(CH_3)_3Si]_2N \overset{+}{-} N[Si.(CH_3)_3]_2$.[101]

The possibility of the approach of the silicon and nitrogen atoms in space with formation of a donor–acceptor bond between them, as in silatranes, is regulated not only by the electronic but also by the steric effects of the substituents R and R' at these atoms in compounds of the type $R_2Si(OCH_2.CH_2)_2NR'$.[102–104] Bulky substituents increase the length (i.e. weaken) of the donor–acceptor bond. Thus, on passing from R' = H to CH_3 and $C(CH_3)_3$, the Si–N distance increases from 2.30 to 2.68 and 3.16 Å respectively.

Analysis of the factors determining the steric structure of the germatranes $RGe(OCH_2CH_2)_3N$ also led Tandura et al.[105] to the conclusion that the degree of transannular interaction between the nitrogen and germanium atoms depends not only on the electronic but also on the steric effects of the substituents R.

Ideas concerning the intramolecular coordination interactions between the E and X atoms (here X has an unshared electron pair), similar to those observed in silatranes and related derivatives, have been invoked also to account for the physical properties of compounds with a simpler structure, for example, those with fragments of the type $Si(CH_2)_nX$.[106] Together with the electronic effects of the substituents at the E and X atoms, the intramolecular coordination [which apparently takes place via a mechanism involving the $(p-d)\sigma$ interaction[106]] is also regulated by steric factors, as shown[107] for X = N (this will be discussed below for other X).

The influence of steric effects in the formation of intermolecular complexes involving compounds with E–N fragments is just as evident. Steric effects play a significant role both in the reactions of vinylsilanes with amines[108] and in the formation of complexes with $SnCl_4$ as acceptor.[109] The enthalpy of complex formation with $SnCl_4$ is determined not only by the electronic effects of the substituents in the Si–N fragments but also by steric factors, which is indicated by the decrease of ΔH in the presence of bulky substituents at the nitrogen atom. The absence of appreciable steric effects in the protonation of the same compounds, i.e. under conditions where there is a sharp decrease of the possible steric hindrance originating from the acceptor in the donor–acceptor complex, is striking.

Systematic investigations of the electron-donating capacity in the formation of hydrogen bonds involving compounds with the Si–N,[110–114] Ge–N,[110,112,114,115] and Sn–N[110,116,117] groups, starting with the first studies by Abel et al.[110] and Pacl et al.,[111] revealed the possible influence not only of electronic but also of steric effects of the substituents attached to these groups. In the study of a hydrogen bond of the type $\geq E-N\cdots H-N\leq$ or $\geq E-N\cdots D-C\leq$ with pyrrole or deuteriochloroform by infrared spectroscopy, the parameter $\Delta\nu$, namely the shift of the stretching vibration frequency of the unassociated pyrrole or deuteriochloroform on formation of a hydrogen bond, was used as a quantitative measure of the electron-donating capacity. This parameter is proportional to ΔH and ΔG for hydrogen bond formation at least in series of isotypical compounds.[118]

The steric shielding of the donor centre (the nitrogen atom) by three substituents should be accompanied by a decrease of $\Delta\nu$ and ΔH and hence of the electron-donating capacity of the compounds. In order to obtain information about the donor–acceptor properties of the substituents R_3E (E = C, Si, Ge, or Sn) in the compounds $(R_3E)_nNR'_{3-n}$ (this was one of the main tasks in the investigations quoted above[110–117]), it is therefore necessary to have information about the influence of the steric effects on $\Delta\nu$.

For certain compounds with E–N fragments, such information has been obtained by correlation analysis in a study,[117] where, together with organoelemental amines, a wide range of organic amines were also considered. Among the latter, there are compounds for which the parameters $\Delta\nu$ [the shift of the ν(C–D) frequency in the infrared spectrum of deuteriochloroform on formation of the $\geq N\cdots D-C\leq$ hydrogen bond] vary linearly with the sum of the inductive constant σ^* of the three substituents at the nitrogen atom, which indicates the virtual absence of steric effects in the formation of the hydrogen bonded complex. The steric effects are insignificant both for the compounds $AlkN(CH_3)_2$ and for $(CH_3)_3EN(CH_3)_2$ (E = Si, Ge, or Sn). However, on passing to compounds with the $N(C_2H_5)_2$ and $N[Sn(CH_3)_3]_2$ fragments, the steric hindrance generated by the substituents at the nitrogen atom prevents the formation of a hydrogen-bonded complex and is responsible for the decrease of $\Delta\nu$.[117] The increased role of steric effects following the accumulation of substituents of the type $(CH_3)_3E$ (E = C, Si, and Sn) at the Group V element is also indicated by NMR data for the compounds $(C_2H_5)_{3-n}\cdot P[E(CH_3)_3]_n$.[119] It follows from these data that the anomalies (from the standpoint of the donor–acceptor properties of the substituents) in the changes in the chemical shift increase with increasing n.

(b) Compounds with E–Group VI Element Fragments

The Si–O–C and Si–O–Si valence angles are known for many organosilicon compounds (see, for example, a number of reviews[120–122]). If it is assumed that these angles are determined by the influence of only the electronic factors of the substituents at the silicon and carbon atoms and that steric effects do not play an appreciable role, a number of contradictions arise. Thus, on passing from $(CH_3)_2O$ (the C–O–C angle is 111°43′ [123]) to Alk_3SiOCH_3 [120] (Alk = CH_3, C_2H_5, or n-C_3H_7) and H_3SiOCH_3,[124] the Si–O–C angle increases to 117–123°, while in the case of $Alk_3SiOC(CH_3)_3$ it amounts to 127° ± 3°.[120] Similarly the angle increases from 121° to 140° on passing from $CH_3OC_6H_5$ to $Alk_3SiOC_6H_5$.[120]

There is no doubt that the main cause of the larger changes in the Si–O–C angles compared with the C–O–C angles is the electronic effects of the silyl substituents, i.e. the electron-accepting properties of the $SiAlk_3$ group compared with the electron-donating properties of the substituents CH_3 or $CAlk_3$. However, steric effects are also significant,[120] which is manifested particularly clearly in the disiloxanes $R_3SiOSiR_3$. The successive transition from R = CH_3 to H, Cl, and F is accompanied by some shortening of the Si–O distance (1.63, 1.63, 1.59, and 1.58 Å respectively) and a significant increase of the Si–O–Si valence angle from 130° ± 10°[125] to 144°,[126] 146°,[127] and 156°,[128] in conformity with the enhancement of the electron-accepting properties of R in this series.

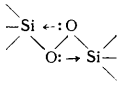
Contrary to the expectation based on the comparatively similar electronegativities of the hydrogen atom and the phenyl and vinyl groups, the Si–O–Si angles in hexaphenyldisiloxane,[129,130] hexavinyldisiloxane[131] and also in $(H_2C{=}CH)_3\cdot SiOSi(C_6H_5)_3$ [131] are 180°. Apparently the main cause of the linear structure of the disiloxane fragment is the large bulk of the substituents, while the packing effects do not exert a decisive influence,[130] although, according to Vlasenko,[131] they do contribute to an increase of the Si–O–Si angle.

A number of instances of the influence of steric effects on the structure of organocyclosiloxanes have been quoted in a review of X-ray diffraction data.[122] The steric effects of two bulky $(CH_3)_3SiO$ substituents in *ortho*-positions in the benzene ring hinder the free rotation about the $O-C_{ar}$ bond, revealed by a change in both the dipole moments[132] and the NMR spectra.[133] Intramolecular coordination interactions between the E and O atoms not linked by direct chemical bonds are well known for organoelemental compounds.

However, it follows from the review of early studies[106,134] that data for intramolecular coordination in silicon compounds are contradictory. It is known[46,55] that, with increase of the effective positive charge on E and also on passing from E = Si to E = Ge and Sn, the energy of the coordinate bonds increases. Therefore there is no doubt about the occurrence of intramolecular interactions in compounds with fragments of

the type SiF_3, $SiF_2(CH_3)$, and $SiF(CH_3)_2$ [135,136] and also for germanium and, even more so, tin[105,106,137] derivatives.

Analysis of the literature data has shown that the coordination interactions between the E and O atoms are influenced (like the intramolecular coordination between E and N) by the steric effects of the substituents linked to the donor and acceptor centres in the molecule. This is shown very clearly for organosilicon peroxides with the fragment



in which intramolecular coordination leads to a decrease of the electron-donating capacity of the oxygen atoms owing to their involvement not only in $(p-d)\pi$ interaction with the neighbouring silicon atom but also in an intramolecular interaction with the more remote silicon atom. With alkyl substitution at silicon, intramolecular coordination is disturbed and the electron-donating capacity of the oxygen atoms increases. This is manifested particularly by a sharp increase of $\Delta\nu$(O–H) on formation of the hydrogen-bonded complexes (>O...HO) with phenol.[138]

The length of the Ge–O intramolecular coordinate bond in compounds with the $O=C-C-C-GeCl_3$ fragments varies from ~2.1 to 3.2 Å.[105] Together with intermolecular interactions, whose influence on the length of the coordinate bond has been considered by Tandura et al.,[105] the energy of this bond is apparently determined also by the influence of the substituents on the geometry of the five-membered rings formed, i.e. by the steric factors. Study of the thermodynamic and kinetic parameters of an intramolecular metallotropic rearrangement (the 1,5-shift of the R_3Ge group between two oxygen atoms in $R_3GeOC(CH_3)=CHC(CH_3=O]$ has shown that formation of a coordinate bond between the germanium atom and the oxygen atom of the CO group is influenced by the steric effects of the substituent R.[139]

The steric effects of the substituents are shown very clearly in the formation of intermolecular complexes with a siloxane or disiloxane group.[121] Thus a decrease of the heat of complex formation with increasing length of the alkyl substituent R and with the degree of its branching was established a comparatively long time ago[140] in studies by the dipole moment, infrared spectroscopic, calorimetric, and cryoscopic methods of the complexes of $SnCl_4$ with the alkoxysilanes $Si(OR)_4$ and $R'Si(OR)_3$. The complex forming capacity also decreases with intensification of the steric effects of the substituents at the silicon atom, which follows from the data obtained in a study of the complexes of $SnCl_4$ with $(R_3SiO)_3PO$.[141]

Whereas compounds containing siloxane linkages show little tendency towards self-association,[121] the formation of intermolecular associated species is an extremely characteristic feature of the related tin and lead compounds and the influence of the steric effects of the substituents is then strikingly revealed. Thus, according to NMR data for tin nuclei, compounds of the type $(C_4H_9)_3SnOAlk$ are monomeric at room temperature and have a tetrahedral tin atom,[142] while the derivatives $(C_4H_9)_2Sn(OAlk)_2$ are monomeric only for Alk = s-C_4H_9 or t-C_4H_9, which prevent dimerisation by virtue of steric factors. The replacement of the butyl group in the OC_4H_9 fragment of the monomeric complex $C_4H_9Sn(OC_4H_9)_3$ by lower alkyl groups leads to a decrease of steric hindrance, the compounds undergo association, and the tin atom becomes hexacoordinate.[142] The bulky substituents R and R' prevent the association of the tin carboxylates $R_3SnOCOR'$ [143] and, when R = $C_6H_5C(CH_3)_2CH_2$, the compounds are monomeric also for R' = H or CH_3.[144,145] The lead derivatives R_3PbX (where X has unshared electron pairs) are highly associated, but in the presence of bulky substituents the compound [for example, $(C_6H_5)_3PbOSi(C_6H_5)_3$ [146]] exists in the monomeric form.

The most systematic information about the influence of electronic and steric effects of substituents at the E–O bond, referring mainly to silicon compounds, has been obtained in the study of the hydrogen bonds with various electron acceptors by infrared spectroscopy and ^1H NMR[121] (although the information about the steric effects has also been obtained by analysing the infrared spectra of individual siloxanes[147]).

Individual correlation lines of the type $\Delta\nu = \Delta\nu_0 + a\Sigma\sigma^*$, representing the correlation between $\Delta\nu$ [the shift of the ν(O–H) frequency of phenol in the formation of hydrogen bonds with the test compounds] and the sum of the inductive constants σ^* of the substituents at the silicon atom have been observed also for the compounds $R_3SiOC_2H_5$, $RSi(OC_2H_5)_3$, $RSi(OCH_3)_3$, and $(R_3Si)_2O$.[148,149] However, a more careful analysis of the parameters $\Delta\nu$ [150,151] as well as the data of Voss et al.[152] and the conclusions reached by Voronkov et al.[121] demonstrated the influence on the electron-donating properties of compounds with the Si–O bond not only by the inductive effect but also by the steric effect of the substituents linked to the silicon and oxygen atoms. For example, on passing from the compounds $X(CH_3)_2SiOC_2H_5$ to $X(CH_3)_2SiOC(CH_3)_3$ (X represents various organic substituents), the electron-donating capacity does not increase (as might have been expected on the basis of the inductive effect) but actually falls.[151,152]

The accumulation of bulky substituents at the atoms of the Si–O or Ge–O fragment results in a dependence of the steric accessibility of the silicon atom in these fragments, as an electron donor centre for the formation of the hydrogen bond, on the size and geometry of the other species involved in the hydrogen-bonded complex. By varying the hydrogen bond acceptor (phenol, pyrrole, deuteriochloroform), it is therefore possible to discover the electron donors which entail steric hindrance in complex formation with the acceptors. Such difficulties are observed, in particular, on formation of hydrogen-bonded complexes with pyrrole by compounds of the type $(CH_3)_3EOE(CH_3)_3$, where E = C or Si,[151] and also $Ge(OC_6H_5)_4$ and $CH_3Ge(OC_6H_5)_3$.[153]

When an even more pronounced steric hindrance is generated at the oxygen atom, for example, on passing to compounds of the type $(C_6H_5)_3SiOSi(C_6H_5)_3$, hydrogen-bonded complexes with the phenol coordinated to the oxygen atom of the Si–O–Si fragment cannot be detected from the infrared spectra,[154] despite the seemingly extremely favourable configuration of this fragment (the angle between the heavy atoms is 180°).[129,130]

Although the steric hindrance in the formation of hydrogen-bonded complexes between alkoxysilanes and deuteriochloroform is apparently weaker than in the case of pyrrole,[151,153] steric effects have also been detected by ^1H NMR in the complexes with chloroform.[121,155,156] The change in the chemical shift in the ^1H NMR spectrum of chloroform on formation of a hydrogen bond with $(CH_3)_3SiOAlk$ depends both on the inductive and steric (E_S) constants of the alkyl substituents and the steric hindrance increases with increasing n in $(CH_3)_{4-n}Si(OC_2H_5)_n$.[156] The comparatively high electron-donating capacity of the cyclotrisiloxanes $(R_2SiO)_3$ compared with compounds having a linear structure or containing larger rings can serve as yet another clear example of the manifestation of steric effects on formation of hydrogen-bonded complexes with phenol. In strained cyclic trisiloxanes, the electron-donating capacity at the oxygen atom increases both as a result of the

improved steric accessibility of these atoms for the formation of the hydrogen bond and the weaker $(p-d)\pi$ interaction in the silicon–oxygen bonds.[157] Bulky substituents at the silicon atom reduce the capacity of silanols with the Si–O–H fragments for the formation of intermolecular hydrogen bonds.[158]

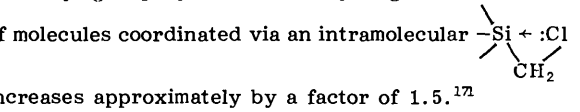
The high efficiency of the NMR method in the study of steric effects [for example in compounds of the type $(CH_3)_3$. .SiOAlk [159]] was recently demonstrated yet again in the systematic investigation of alkoxysilanes by ^{13}C, ^{29}Si, and ^{17}O NMR.[160–162] It was established that the chemical shifts of the signals in the NMR spectra of mono-, di-, tri-, and tetraalkoxysilanes are determined by the joint influence of the inductive and steric effects of the substituents. The role of the steric effect increases with increasing number of alkoxy-groups at the silicon atom, in conformity with the results obtained by the other research techniques examined above. Steric effects can influence also the chemical shifts in the NMR spectra of alkoxygermanes.[161,163] According to NMR data,[164] in compounds with the $(CH_3)_3Si–O–C=C$ fragments, the conformations in which conjugation between the oxygen atom and the double bond is reduced are preferred owing to the steric effects of the trimethylsilyl group.

(c) Compounds with the E–Group VII Element Fragments

There is limited information in the literature about the influence of steric effects on the complex-forming capacity and physical properties of compounds with such fragments. An infrared spectroscopic study of hydrogen bonding with phenol in compounds of the type $R_3E–Cl...H–O–C_6H_5$ and $R_3ECH_2Cl...H–O–C_6H_5$ failed to reveal[165] anomalies which could not be accounted for by the electronic effects of the substituents at the chlorine atoms and would require allowance for steric effects. However, it does not follow from this that steric effects are completely absent from compounds of the type considered, since careful analysis of the ^1H NMR spectra of derivatives of the type $(n-C_3H_7)_3ECl$, where E = Si, Ge, or Sn, indicates the presence of steric hindrance to free rotation about the C–E bonds, which increases in the sequence Sn < Ge < Si.[166]

The free rotation about the Si–C bond is hindered also in $[(CH_3)_3C]_3SiX$, the barrier increasing from 6 to 8.5 kcal mol^{-1} with increase in the size of X in the sequence H < Cl < Br < I.[167] There are indications of a dependence of the complex-forming capacity of the compunds R_nSiCl_{4-n} (R = CH_3 or C_2H_5, n = 0–4) in relation to acetone on the bulk of the substituents at the silicon atom.[168]

Steric effects exert an appreciable influence on the intramolecular coordination between the silicon and chlorine atoms not linked by a direct chemical bond in compounds containing the $SiCH_2Cl$ fragments.[106] Such intramolecular interactions, which have already been partly examined above, are intensified with increase of the atomic number of the element E and with increase of its effective positive charge. Under conditions close to the most favourable ones, for example, in the case of $Cl_3SnCH_2CH_2CH_2Cl$,[169] the presence of a coordinate bond was therefore demonstrated by direct experiments. In silicon compounds this kind of bond is fairly strong only in the presence of three acceptors—the fluorine atoms at the silicon atom,[135] the enthalpy of formation of the coordinate bond diminishing after the replacement of the fluorine atoms by methyl groups,[135] and in $(CH_3)_2(ClCH_2)SiH$ it amounts to only ~1 kcal mol^{-1}.[170]

At the same time the weak coordination interactions in compounds with the $E–CH_2Cl$ fragments (E = Si or Ge)[171,172] exhibit a distinct dependence on both the electronic[170–172] and steric[171] effects of the substituents at the atom E. Thus, on passing from Alk_2HSiCH_2Cl to $AlkH_2SiCH_2Cl$, i.e. on replacement of the alkyl group by the smaller hydrogen atom, the number of molecules coordinated via an intramolecular  linkage increases approximately by a factor of 1.5.[171]

(d) Compounds with E–Ar Fragments

The results of X-ray diffraction studies indicate appreciable steric effects in tetra-aryl derivatives of silicon subgroup elements. Thus, apparently owing to the steric hindrance generated by the four substituents at the silicon atom, the Si–C bond length (1.872 Å[173]) in tetraphenylsilane is greater than in phenylsilane (1.843 Å).[174] Steric hindrance at the central atom increases after the introduction of methyl groups in the *ortho*-position in the benzene ring. Thus, on passing from tetraphenylgermane to tetra(o-tolyl)germane, the Ge–C bond length increases from 1.957 Å to 1.966 Å,[175,176] while in the corresponding tin derivatives the Sn–C bond length increases from 2.144 Å to 2.160 Å.[177]

Anomalous valence angles are also observed at the central atom. These anomalies are particularly marked for the mesityl derivatives in which the aromatic rings contain two *ortho*-methyl substituents. The angles between the Mes–E–Mes bonds in the compounds Mes_3EH with E = C, Si, or Ge (Mes = mesityl) are respectively 118.3°, 116.0°, and 115.5°, i.e. they increase with decrease of the atomic number of E and with increase of the steric hindrance of the atom of the latter.[30,178] The conformation in which the mesityl substituents are arranged around the silicon or germanium atom in a propeller fashion corresponds to the minimum steric strain.[179] The barriers to internal rotation about the E–Mes bonds in Mes_3EH, which amount to 8.3, 6.0, and 3.1 kcal mol^{-1} for E = Si, Ge, or Sn respectively, apparently agree with the hypothesis of a predominant contribution to these quantities by steric interactions of the *ortho*-substituents in the neighbouring aromatic rings[179] (see also Refs. 180 and 181).

The anomalies discussed above, observed for the mesityl derivatives, are clearly manifested in their infrared spectra. Thus the frequencies and intensities in the E–H (E = Si or Ge) stretching vibration bands in the infrared spectra of Mes_3EH are extremely unusual.[182] For the vast majority of the substituents R in R_3EH, the mode of the E–H bond vibrations remains unchanged, since the substituents R influence the frequency and intensity of this highly characteristic vibration only via their electronic effects. The pronounced steric hindrance in mesityl derivatives leads to the disturbance of the mode of the given vibration and to a change in the conditions for the $(p-d)\pi$ interaction of the atom E with the aromatic ring.[182] As a result, the frequency and intensity of the E–H bond vibration no longer depend solely on the electronic effects. These anomalies are more marked for silicon derivatives than for germanium derivatives.

It follows from the NMR data for the compounds Ar_3ER, where R are various organic substituents, and Ar_4E, where E = Si, Ge, or Sn, that the activation energy for the intramolecular rotation of the aryl groups is determined both by the presence of *ortho*-substituents in the aromatic rings and by the size of the atom E.[183] Steric effects in compounds of this type make a significant imprint also on their reactivity. Thus the substitution of bromine in the bromo-derivatives of triarylgermanes and triarylstannanes with methyl substituents in the *o*-position is inhibited by steric factors to a lesser extent in the organotin compounds as a consequence of the smaller size of the tin atom compared with the germanium atom.[184]

It was established comparatively long ago[43] that the accumulation of bulky organic substituents in the aromatic ring alters significantly the thermodynamic characteristics of the charge-transfer complexes of benzene derivatives even with comparatively smaller acceptor molecules such as those of iodine chloride. In particular, this is shown by a sharp decrease of the equilibrium constant of the complex-formation of 1,3,5-tri-t-butylbenzene and to an even greater extent hexaethylbenzene, compared with the less sterically hindered alkylbenzenes. The entropy of formation of the hexaethylbenzene–iodine complex as well as the equilibrium constant are low. The acceptor apparently does not overcome the steric barrier established by the bulky substituents and is located at a distance from the donor, which is greater than the optimum distance for the donor–acceptor interaction.[43]

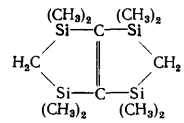
It is noteworthy that the equilibrium constant is more sensitive to steric effects than, for example, the frequency of the charge-transfer band ν_{CT} in the ultraviolet spectrum of the complex. For this reason, no anomalies associated with the steric factors are observed in the values of ν_{CT} for a series of compounds $C_6H_5CH_{3-n}[Si(CH_3)_3]_n$ (n = 1–3) and the equilibrium constant diminishes with increase of n (i.e. the size of the ring substituent).[185] However, with increase of the number of t-butyl or trimethylsilyl substituents in the ring, whereupon the role of the steric effects increases, anomalies do appear also in the values of ν_{CT}. This is manifested, in particular, by a decrease of the electron donating capacity of substituted phenols containing such groups in the formation of complexes with tetracyanoethylene.[186]

Like the decrease of the complex formation constants, the decrease of the electron-donating capacity is associated (for a molecule of a benzene derivative with bulky substituents) with the impossibility of realising the potential electron-donating properties because of the steric hindrance in the approach to the acceptor molecule to the optimum distance for electronic interactions of the complex. The fact that the distance actually attained exceeds (for steric reasons) the optimum distance can be formally regarded as a decrease of the electron-donating capacity. For this reason, the frequency ν_{CT} in the ultraviolet spectra of complexes of phenol derivatives having two or three bulky substituents [$C(CH_3)_3$, $Si(CH_3)_3$, $Ge(CH_3)_3$] with tetracyanoethylene ceases to be satisfactorily correlated with the σ^+ constants of the substituents.[186,187] This shows that both the electronic and steric effects are important in the formation of complexes by compounds of this kind. When bulky substituents are introduced into the phenol molecule (in the *ortho*-position relative to the hydroxy-group), the electron-accepting capacity of the compound in the formation of a hydrogen bond with tetrahydrofuran diminishes due to steric hindrance.[186]

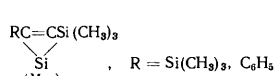
Extremely clear results have been obtained by yet another method for the estimation of the steric effects of substituents in benzene derivatives, which is based on analysis of the correlations between the ionisation potentials I_D, characterising the energy of the highest occupied molecular orbital (HOMO), and the charge-transfer band frequencies ν_{CT} in the ultraviolet spectra of the complexes of these derivatives with tetracyanoethylene.[188] It follows from the general theory[32] of charge-transfer complexes that there should be a linear relation between I_D and ν_{CT}; this has been frequently confirmed experimentally,[39] especially for compounds with related structures.[189] However, with increase of the number of organoelemental substituents in the benzene molecule, the linear relation between I_D and ν_{CT} ceases to hold. Thus, for the compounds $C_6H_{6-(m+n)}(CH_3)_m[CH_2Si(CH_3)_3]_n$ ($m+n$ = 1–6), the points on the plot corresponding to the hexasubstituted derivatives of the type $C_6[CH_2Si(CH_3)_3]_6$, $C_6(CH_3)_4[CH_2Si(CH_3)_3]_2$, $C_6(CH_3)_3[CH_2Si(CH_3)_3]_3$, and also $C_6H_2[CH_2Si(CH_3)_3]_4$ deviate from the linear relation between I_D and ν_{CT} towards higher values of ν_{CT}, i.e. the electron-donating capacity falls due to the steric hindrance to complex formation with tetracyanoethylene.

According to the ionisation potentials of sterically hindered benzene derivatives,[188] the steric hindrance influences also the effects of the conjugation of the substituents with the ring; these results will be examined in the next Section of the review.

A number of anomalies have also been observed in the properties of sterically hindered ethylene derivatives.[20,42] Thus the ring strain in the compound



leads to an increase in the length of the multiple bond and alters the valence angles.[190] The accumulation of bulky substituents at the C=C bond is accompanied not only by an increase in its length but also by the twisting of this bond. Thus the C=C bond lengths are respectively 1.368 and 1.370 Å and the tortional angles are ~30° and ~50° in $[(CH_3)_3Si]_2C{=}C[Si(CH_3)_3]_2$ [191] and in the sterically even more hindered $[(CH_3)_3Si]_2C{=}C[Si(CH_3)_2C(CH_3)_3]_2$.[192] The sharp decrease of the reactivity of the silacyclopropenes



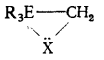
is caused by the presence in the molecule of the two bulky mesityl substituents.[193,194] It is noteworthy that electronic factors also influence the stability of compounds of this type.[195–197]

(e) The Central Atom E as the Acceptor Centre and the E–C Bond as the Donor Centre in Complex Formation

In contrast to carbon compounds, complex formation via the central atom E is characteristic of derivatives of silicon subgroup elements.[6,8,34,46,55,106] In complex formation of this type, the atom E functions as a ν-acceptor, apparently by virtue of its unoccupied *nd* orbitals.[47,55] The possibility of the realisation of the potential ν-acceptor properties (determined by the nature of the atom E and the electronic effects of the substituents linked on it) depends also on the steric shielding of the atom E by these substituents and on the steric situation at the donor centre of the donor molecule. In the absence of the complicating influence of steric effects, the ν-acceptor capacity increases with increase of the atomic number of E (on passing from Si to Ge, Sn, and Pb) and with increase of the effective positive charge on E, which is ensured by the addition of electron-accepting substituents to E.[55,106] The influence of steric effects is manifested both by the breakdown of these characteristics of complex formation and by the anomalous thermodynamic characteristics of the complexes.

Although the complex-forming capacity of silicon compounds is the smallest among all the derivatives of the elements E, it has been established by infrared spectroscopy[198] that even triethylsilane is solvated specifically by electron-donating solvents and that steric effects are then manifested to an appreciable extent. These effects are smaller for oxygen-containing solvents than for nitrogen-containing solvents, in which the donor centre (the nitrogen atom) is more shielded by the substituents. On passing from triethylsilane to triethylgermane, the solvation intensifies, but the steric effects in the formation of donor–acceptor complexes hardly change.[198]

It is striking that, judging from the infrared spectra, a fairly profound analogy is observed between the formation of the solvate complexes $R_4E...L$, where L is an electron donating solvent,[198] and the intramolecular coordination of the type



examined above.[106,170-172] The analogy holds also from the standpoint of the steric effects of E and the substituents R linked to L in complex formation. In addition, competition between these two types of complexes is well known.[170-172,199] With increasing electron-donating capacity of L or with increase of the concentration of the latter in solutions, the intramolecular coordination probably breaks down and the concentration of the solvates $R_3(XCH_3)E...L$ rises; however, the role of the steric effects under these conditions has been inadequately studied.

Another form of simultaneous complex formation via two possible pathways is known for the phenyl derivatives of silicon and germanium.[200-202] These compounds can exhibit both π-donor (by virtue of their aromatic rings) and ν-acceptor [by virtue of the atoms E (Si, Ge)] properties in relation to molecular oxygen. It has been shown by the method of the low-temperature quenching of luminescence that in the phenyl derivatives of silicon only the π-donor capacity is realised and the steric effects are then insignificant. Phenyl derivatives of germanium behave as both π-donors and ν-acceptors in complexes with molecular oxygen. In the latter case the equilibrium constant of the complex formation reaction depends markedly on the steric effect of the substituents linked to the germanium atom. It increases, for example, on passing from $(C_6H_5)_4Ge$ to $C_6H_5GeH_3$ by a factor greater than 20,[200,202] although these compounds have similar π-donor capacities and apparently identical charges on the germanium atom.

Compared with silicon and germanium compounds, tin derivatives have more pronounced ν-acceptor properties; in addition, a higher sensitivity of these properties to the influence of substituents at the central atom is characteristic of these compounds. Therefore the study of the donor–acceptor complexes involving tin compounds yielded extremely clear information about the steric effects in the donor and acceptor molecules. Thus calorimetric investigations of the complexes $Alk_{4-n}SnCl_n$ with different N- and O-donors established an increasing enthalpy of complex formation (i.e. of the strength of the donor–acceptor bond) with increase of n.[203]

At the same time a significant dependence of ΔH and of the composition of the complex on the steric hindrance in the donor molecule has been observed.[203] For donors generating an intense steric hindrance, for example, $(C_4H_9)_3N$, even the strongest acceptor $SnCl_4$ forms complexes in which the donor: acceptor ratio is 1:1 (and not 2:1).[203] The influence of the steric effects of the alkyl groups in tetra-alkylstannanes is very strong in the formation of complexes with molecular oxygen,[204] iodine,[205-208] and tetracyanoethylene.[37] It has been established by the method of low-temperature quenching of luminescence, even in relation to the comparatively weak complexes with molecular oxygen, that the equilibrium constant of complex formation decreases with increase of the size of the alkyl group in the tetra-alkylstannanes in the sequence $CH_3 > n\text{-}C_4H_9 > n\text{-}C_5H_{11}$.[204]

For the stronger charge-transfer complexes with iodine and tetracyanoethylene (acceptors), in which the Sn–C bond having a comparatively low ionisation potential (8.2–9.7 eV[37]) functions as the donor, the influence of steric effects has been studied very thoroughly. It has been shown that comparison of the ionisation potentials of the compounds Alk_4Sn, obtained by photoelectron spectroscopy, and the ultraviolet spectra of the complexes of these compounds with iodine[205-207] and tetracyanoethylene[37] permits a quantitative estimation of the steric effects of the alkyl groups at the tin atom.

In these studies it has also been established that the steric effects influence not only the formation equilibrium constant of the charge-transfer complex[206] but also the rate constants for the subsequent process, for example the insertion of tetracyanoethylene in the tin–carbon bond in Alk_4Sn.[37] Under these conditions, both in the formation of the complex and in its subsequent reaction, the character of the influence of the steric effects does not change qualitatively. In both cases these effects intensify if the alkyl groups are replaced in the sequence $CH_3 \ll C_2H_5 < iso\text{-}C_3H_7 < iso\text{-}C_4H_9 < t\text{-}C_4H_9$; in contrast to other tetra-alkylstannanes, tetraneopentyltin, in which the central atom is most shielded by bulky substituents, does not react with tetracyanoethylene.[37] On the other hand, the increase of the size of the central atom on passing to lead compounds and the increase of the E–C interatomic distance should reduce steric hindrance, which is in fact observed for the complexes $(CH_3)_{4-n}(C_2H_5)_nPb$ with tetracyanoethylene.[37]

The equilibrium constants of the complex formation reactions of tetra-alkylstannanes with iodine, complicated by the steric effects of the bulky alkyl groups, are comparatively low.[207] The constants are very much greater for the formation of charge-transfer complexes between iodine (acceptor) and Alk_3SnX, where X = Br or I (donors).[209] In contrast to tetra-alkylstannanes, in this case the hydrogen atom X functions as the donor centre in complex formation and not the tin–carbon bond.[209,210]

It is to be expected that the role of the steric effects in complexes involving tetra-alkyl derivatives of silicon or germanium as well as compounds containing the silicon–silicon and germanium–germanium fragments as donors is greater than in tetra-alkylstannanes and distannanes. However, systematic studies of this kind have not been carried out and there exist only fragmentary factual data on the spectra of the complexes.[39,211] Appreciable steric effects are manifested in cyclic polysilanes.[212,213] Thus the polysilane $[(CH_3)_3C(CH_3)Si]_4$ whose electronic transition band occurs at an extremely high wavelength and which has a very low ionisation potential is nevertheless resistant to oxidation. The unusual properties of this compound are caused not only by electronic but also by steric effects of the four t-butyl substituents.[212,213]

Anomalously long Si–Si and Si–C bonds are observed in cyclotrisilanes $(R_2Si)_3$ with bulky substituents R: 2,6-dimethylphenyl,[214] neopentyl,[215] and t-butyl.[216]

Important information about steric interactions between the silyl substituents and saturated cyclic systems,[217] including highly strained silacyclopropane derivatives,[218] has been obtained by ^{29}Si NMR.

2. The Influence of Steric Effects on Conjugation in Compounds of Silicon Subgroup Elements

As shown above, the presence of bulky substituents in the donor and/or acceptor molecules exerts a significant influence on the spectroscopic and thermodynamic characteristics of DA complexes.

Steric factors can influence the donor and acceptor centres of the complex by regulating the degree to which these centres approach one another in complex formation, as a result of which the potential complex-forming capacity is not fully realised. Furthermore, steric effects can alter the electronic intermolecular interactions already in the initial

donor or acceptor molecules. As an example, one may quote the steric inhibition of conjugation[2,4,13] or, conversely, the establishment of favourable conditions for conjugation[42] in the molecule. These phenomena, which are well known for organic compounds,[2,4,7,13,15,45] are observed also in organoelemental chemistry.[42]

We shall consider the influence of steric factors on the extremely specific effects of the $(p-d)\pi$ interaction and hyperconjugation, especially for compounds of the silicon subgroup elements. The problem of the $(p-d)\pi$ interaction with participation of the unoccupied *nd* orbitals of the E atoms has been studied in detail.[46,47,53-55] It follows from these studies that the π-acceptor properties of the atoms E in relation to the substituents X (an atom with unshared electron pairs or an αβ-unsaturated hydrocarbon group), which have been thoroughly investigated experimentally, can be interpreted as $(p-d)\pi$ interaction in the E–X fragments via the partial transfer of electron density from the atom X to the unoccupied *nd* orbitals of the atom E. Under these conditions, the E–X bond acquires partial double bond character and the degree of the latter depends on the ratio of the electron-donating properties of the atom X and the electron-accepting properties of the atom E. The ratio of these properties in the atoms involved in the E–X bond depends in its turn on the other substituents attached to the bond.

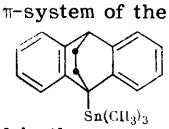
From the standpoint of the influence of stereoelectronic factors on $(p-d)\pi$ interaction, it is possible to consider two cases. The first case is that of compounds of the type R_3EX in which the substituents R are incapable of forming $(p-d)\pi$-bonds with E, i.e. the molecule has only one substituent X involved in the $(p-d)\pi$ interaction with E. In this case it has been shown for E = Si[219] and Ge [220] that the relative capacity of the substituent X for the formation of $(p-d)\pi$-bonds with E is determined exclusively by the resonance constants σ_R,[46] characterising the conjugation of these substituents with the benzene ring and a double or triple bond.[221] This confirms yet again the profound analogy, established a long time ago,[49] between the conjugation effects in organic and organoelemental systems and also the wide-scale applicability of the constant σ_R as a quantitative measure of these effects.

The second case is that of compounds of the type R_2EX_2, REX_3, and EX_4 with several substituents X involved in the $(p-d)\pi$ interaction with the atom E. In such compounds two additional factors (compared with the derivatives R_3EX) influence the $(p-d)\pi$ interaction in the molecule, namely the effective charge on E, which depends on the inductive and mesomeric effects of X, and the overlap integral of the interacting p_π and d_π orbitals of the atoms X and E. The complex situation arising in the $(p-d)\pi$ interaction of the atom E with several atoms X is associated, in particular, with the impossibility of the interaction of E with each of the several X just as strong as with a single X in the molecule. Indeed, as a result of the difference between the valence angles in the molecule (~109.5°) and the angles between the maximum intensity vectors of the d_π orbitals (90°), the interaction of E with several X takes place if the orientation of the d_π orbitals is such that it does not ensure the maximum overlap integrals of the p_π–d_π type in any of the E–X bonds.[53] This is one of the two causes (the second cause is the change in the effective charge on the atom E under the influence of X) of the non-additive dependence of the overall effect of the $(p-d)\pi$ interaction in the molecule on the number of substituents X linked to E. For example, the group overlap integrals of the EX_2 fragment are linked to the two-centre integrals (*s*) of the E–X bonds by the relation $S = (\frac{4}{3})^{1/2}s$.[53]

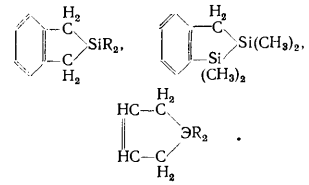
Analysis of the dependence of the frequencies of the highly characteristic stretching vibrations of the E–H bonds in the infrared spectra of the derivatives $AlkX_2EH$, where E = Si [222] or Ge,[220] on the electronic effects of the substituents has shown that, only when account is taken of the above relation between the group and two-centre integrals, is it possible to derive information from spectroscopic data about the influence of the purely electronic factors on the strength of the $(p-d)\pi$-bonds in the EX_2 fragment. In particular, the important conclusion has been reached that the degree of the $(p-d)\pi$ interaction increases with increase of the effective positive charge on the central atom E (Si, Ge).[220,222]

The resonance hyperconjugation effect and particularly its most thoroughly studied variety, namely σ,π-conjugation, are subject to an even more pronounced influence by stereoelectronic factors than $(p-d)\pi$ interaction.[42] By means of a specific alteration of the molecular geometry, it is possible to ensure virtually any spatial disposition of the orbitals interacting via the σ,π-conjugation mechanism and hence achieve both the maximum manifestation of these effects and any of its intermediate values up to its complete absence. Such extensive possibilities for the variation of the effect can be accounted for by the following characteristics of the σ,π-conjugation. The σ,π-conjugation is most pronounced for the maximum overlap of the π orbital of the E–C bond with the π orbital of the C–C or Ar group in compounds with the E–C–C–C or E–C–Ar fragments. Such overlap is attained when the E–C bond and the axis of the π orbital are arranged coplanarly, i.e. when the E–C–C angle is 90°. It has been demonstrated unambiguously for benzyl and allyl derivatives of mercury that the Hg–C–C angle is close to 90°.[223-225] Spectroscopic studies of similar derivatives of silicon subgroup elements have also supported unambiguously similar values of the E–C–C angle,[51,226,227] although direct X-ray diffraction measurements have not in fact been carried out.

Detailed analysis[42] of the factors determining the σ,π conjugation has shown that, in the compounds R_3E-CH_2-X, where X is an αβ-unsaturated substituent, the above conjugation intensities with increase of the electron-donating capacity of R and the electron-accepting capacity of X, with increase of the atomic number of E, and also in the presence of a positive charge on the orbital of the substituent X. The same factors regulate the degree of the σ,π conjugation also in compounds with a more complex structure, where the molecular geometry can ensure the approach of the angle E–C–C to 90°; for other molecular conformations, σ,π conjugation breaks down. Thus the rigid fixation of the Sn–C bond in the nodal plane of the π-system of the compound[51]



and the analogous bond in the corresponding organomercury compound[228] (see also Baidin et al.[229]) leads to the complete breakdown of the σ,π conjugation. For the same reasons, there is no σ,π conjugation in compounds containing planar rings:[230-233]



It is striking that an increase in the size of the rings, accompanied by their conformational non-rigidity, leads to the formation of conformations in which sterically favourable conditions arise for σ,π conjugation (for further details, see the earlier review[42] and in the case of organopolysilanes also Sakurai[234]). Extremely important information about the characteristic features of σ,π conjugation has been obtained for

"sterically overloaded"[40,188,235,236] benzene derivatives $C_6H_{6-n}[CH_2Si(CH_3)_3]_n$. With increase of the size (n) of bulky substituents, the requirement necessary to ensure conditions most favourable for the conjugation of these substituents with the ring break down, which is manifested in the photoelectron spectra and the EPR spectra of the radical-cations of these compounds.[40,188,235] The degree of σ,π conjugation then depends on the angle between the C–Si bond and the plane of the benzene ring or the axis of the C=C bond (for the corresponding ethylene derivatives[41,237,238]). In the latter case, when the sterically most favourable conditions for σ,π conjugation have been created, having fixed rigidly in space the fragments involved in the conjugation, it is possible to obtain ethylene derivatives with very low ionisation potentials (less than 7 eV[41]). Such high electron-donating capacity of compounds of this kind is caused by the maximum extent of σ,π conjugation; for this reason, one observes in this instance a kind of enhancement of conjugation as a result of the creation of the most favourable steric conditions.[41]

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Thus, on the one hand, studies designed to create a general theory of steric effects in chemistry are being prosecuted at the present time. Fundamental advances on these lines will apparently become possible only after a set of specific quantum-chemical investigations have been carried out; so far this problem is far from being solved. On the other hand, a planned general interpretation of an increasing amount of experimental data is being carried out in organic and organoelemental chemistry, which has led, in particular, to the development of empirical methods for the estimation of steric effects and also to the understanding of the specific features of the more varied role of these effects in organoelemental compounds.

Compounds of the silicon subgroup elements are used (at least in the chemistry of non-transition elements) as important model systems for the investigation of the steric effects both in the ground electronic state and (judging from the extensive data on reactivities which have not been included in this review) in the transition state. Together with their independent importance, spectroscopic investigations of the steric effects in the ground electronic states of such model compounds can have a direct bearing on the study of reactivity, since it has been shown for a series of organoelemental systems, for example, for tetra-alkylstannanes,[37] that steric effects in the ground and transition states differ little. Improvement of the spectroscopic research techniques for the primary stages of not too fast reactions involving organoelemental compounds is therefore likely to be useful for the prediction of the influence of steric effects on reactivity.

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Advances in the Chemistry of Organolanthanides

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The results of studies on the synthesis, structure, and reactivity of organometallic derivatives of the lanthanide elements are surveyed. Data concerning their practical applications are presented.
The bibliography includes 235 references.

CONTENTS

I. Introduction	802
II. Hydrides	802
III. Compounds with a lanthanide-carbon σ-bond	803
IV. π-Complexes of organolanthanides	805
V. Compounds with an Ln-E bond	808
VI. Other compounds	811
VII. Applications of organolanthanides	811

I. INTRODUCTION

The chemistry of organometallic derivatives of the lanthanides began to develop vigorously after the characteristics of the formation of organic derivatives of d elements had been elucidated in broad outline. In the last decade an increasing number of investigators have turned their attention to this little studied field in the search for new highly effective stereospecific and regioselective catalysts. Since 1975, Soviet chemists have taken an active part in the development of methods of synthesis of new types of organometallic derivatives of the lanthanides[1,2] although physicochemical studies on the known cyclopentadienyl complexes had been made earlier in our country.[3,4]

The first organometallic lanthanide compounds isolated and reliably characterised were the cyclopentadienyl complexes obtained in the middle of the 1950's.[5,6] Compounds of this type remained for a long time the only ones known for the lanthanides. However, at the present time virtually all classes of organic derivatives of the lanthanides (Ln), also known for transition metals, have been synthesised, including the hydrides, the carbonyls, the σ-alkyl and σ-aryl compounds, the carbonyl derivatives, and the dienyl, allyl, indenyl, cyclo-octatetraenyl, and other complexes. Organometallic derivatives containing an Ln–E bond, where E = nitrogen, phosphorus, oxygen, sulphur, selenium, mercury, boron, germanium, or tin, as well as complexes in which the lanthanide is present in combination with molybdenum tungsten, cobalt, manganese, and rhenium have been synthesised. Carbon-containing clusters with an Ln–Ln bond have been obtained. Only the arene complexes of the lanthanides apparently remain unknown.

In the study of the properties of organometallic derivatives of the lanthanides, their high catalytic activity in the polymerisation of olefins and especially dienes was discovered. In recent years processes have been discovered in which organolanthanides play the role of activators of hydrogen and carbon monoxide and dioxide. All these facts indicate great potential possibilities of the derivatives of *f* elements in catalysis.

The main distinctive factor determining the catalytic activity and specific properties of the compounds considered is the presence of a completely or partly filled 4*f* sublevel in the lanthanide atoms. A detailed discussion of the characteristics of the electronic structure of the lanthanide complexes is found in another review[7] and the literature quoted therein. Here we shall only note the principal characteristics which determine the behaviour of the free lanthanides and their organic derivatives in chemical reactions.

All the 15 elements which follow barium in Mendeleev's Table are electropositive metals. Their normal electrode potentials (+2.522–2.255 V) are close to those of the alkali metals. Accordingly, the organic complexes of the lanthanides are as a rule ionic and exhibit clearly the properties of Lewis acids. The most characteristic oxidation state is Ln^{3+}. Only three elements, namely samarium, europium, and ytterbium, form stable bivalent derivatives, although the Ln^{2+} state is known for all the lanthanides.[7,8] Organometallic compounds with the quadrivalent metal (Ln^{4+}) are known only for cerium. The high ionic radius (0.848–1.061 Å) characteristic of the lanthanides is responsible for their high coordination numbers (up to 12). Compounds with an octacoordinate lanthanide atom are the most common.

A series of reviews,[7,9–17] a collection of articles,[8] and a chapter in one of the books of the "Methods of Organoelemental Chemistry" series[18] have been devoted to organometallic derivatives of the lanthanides. However, the available information in this field has been increasing so rapidly that at the present time it is already felt that a systematic survey of the accumulated data is necessary. In the present review we attempted to examine as fully as possible advances in the chemisty of the organic derivatives of the lanthanides in the field of synthesis and reactivity, including catalytic processes, during the last 5–7 years (up to 1984 together with a few later studies). In addition, data are presented on the synthesis and properties of the phthalocyanide complexes and alkoxides of the lanthanides. In order to create an integral picture of the modern organometallic chemisty of the lanthanides, the review includes a series of earlier studies as well as data for scandium and yttrium compounds.

II. HYDRIDES

The lanthanide hydrides LnH_2 and LnH_3 are readily formed when the free metals are saturated with hydrogen at room temperature.[19] They are usually isolated in the form of powders but, at an elevated temperature, it is possible to obtain crystalline specimens. Heating the hydrides decomposes them into the initial elements. The decomposition temperature depends strongly on the metal: CeH_3 is the least stable (decomposition temperature 157 °C) and LuH_3 is the most stable (decomposition temperature 416 °C). All the

hydrides, with the exception of ScH_2, are rapidly oxidised in air. Water decomposes the trihydrides, LnH_3, at an appreciable rate; the dihydrides LnH_2 are hydrolytically more stable.

Unstable variable-composition hydrides LnM_xH_y are formed when lanthanide melts containing various metals (Mg, Al, Mn, Fe, Co, Ni, etc.) are saturated with hydrogen.[19] The tetrahydroborates $Ln(BH_4)_3$ and the extremely unstable tetrahydroaluminates $Ln(AlH_4)_3$ are obtained in the reactions of the salts LnX_3 with $MM'H_4$ (M = Li or Na; M' = B or Al).[20,21]

The first communication about the synthesis of organometallic complexes containing an Ln–H bond appeared in 1974.[22] It stated that Cp_3CeCl and Cp_2CeCl_2 ($Cp = \eta^5$-C_5H_5) afford respectively Cp_3CeH and Cp_2CeH_2 on interaction with sodium hydride in boiling tetrahydrofuran (THF). The structure of these products was confirmed by elemental analysis and infrared spectroscopy (the bands in the region of 2040 cm^{-1} were assigned to the Ce–H bond vibrations).

The lutetium hydride $Cp_2LuH.THF$ was obtained in two ways:[23]

$$Cp_2Lu{-}R\cdot THF + H_2 \xrightarrow[50\ bar]{} Cp_2Lu{-}H\cdot THF + RH,$$
$$R = CH_2Ph,\ CH_2SiMe_3;$$
$$Cp_2LuCl\cdot THF + NaH \xrightarrow[20^\circ]{} Cp_2Lu{-}H\cdot THF + NaCl.$$

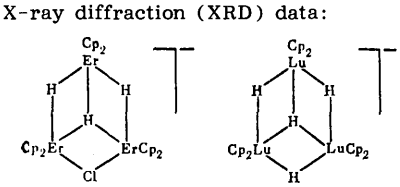
It has been stated[23] that the frequencies ν(Lu–H) and ν(Lu–D) in the infrared spectra of the product and its deuterio-analogue are 770 and 720 cm^{-1} and 540 and 510 cm^{-1} respectively. Apart from elemental analysis, the structure of the hydride has been confirmed by its reaction with Me_3SiCl, which gave rise to trimethylsilane and Cp_2LuCl.

The use of t-butyl derivatives in the synthesis of the hydrides by the hydrogenolysis of the Ln–R σ-bond made it possible to carry out the reaction at atmospheric pressure:[24,25]

$$2(RC_5H_4)_2Ln\text{-}Bu\text{-}t.\cdot THF + 2H_2 \rightarrow [(RC_5H_4)_2Ln{-}H\cdot THF]_2 + 2t\text{-}BuH;$$
$$Ln = Y,\ Er,\ Lu.$$

The deuterio-derivatives have been synthesised analogously. Bands in the ranges 1350–1240 and 975–900 cm^{-1} respectively have been assigned to the Ln–H and Ln–D vibrations in the compounds obtained. X-Ray diffraction analysis of the yttrium dimer $[(MeC_5H_4)_2YH.THF]_2$ and the samarium dimer $[(Me_5C_5)_2SmH]_2$ dimer confirmed the presence of bridging hydrogen atoms, although their coordinates were not accurately established. The differences between the properties (infrared and ^1H NMR spectra and solubility) of the lutetium complex synthesised by Evans and co-workers and the hydride described by Schumann and Genthe[23] led Evans and co-workers[24,25] to the conclusion that the hydride has a different structure.

The dimeric hydrides $(Cp_2LnH.THF)_2$ are also formed on thermal decomposition of the same t-butyl complexes at 20–75 °C via the mechanism of the β-hydride decomposition.[24] It is of interest that thermolysis in the presence of a small amount of LiCl leads to the formation of other products. The erbium complex afforded a product having the composition $\{[Cp_2ErH]_3Cl\}[Li.(THF)_4]$ containing the trinuclear anion (A) according to X-ray diffraction (XRD) data:



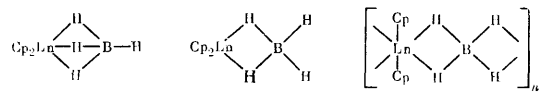
(A) (B)

The analogous anion (B), free of chlorine, has been obtained in the thermolysis of Cp_2Lu–Bu-t.THF.[24] The hydride band in the infrared spectra of the anions (A) and (B) is observed in the region of 1200 cm^{-1}.

The formation of the bivalent ytterbium hydride BuC ≡ CYbH is postulated in the initial stage of the reaction of atomic ytterbium cocondensed with hex-1-yne at 77 K.[26] This complex multistage process leads ultimately to the oligomer $[(BuC \equiv C)_3Yb_2H]_n$. Under the same conditions, samarium gives rise to a product for which the formula $[(C_6H_9)_2SmH]_n$ has been suggested.

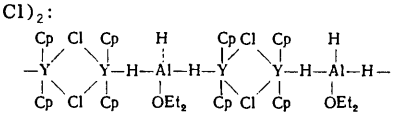
The chemical properties of the lanthanide hydrides are similar to those of the organohydrides of electropositive transition metals. They are hydrolysed by water and D_2O to H_2 or HD respectively and readily exchange hydrogen for a halogen on interaction with RX (R = CCl, Me, or Me_3Si). The yttrium hydrides $[(RC_5H_4)_2YH.THF]_2$ combine with two equivalents of t-butyl isocyanide, giving (according to XRD data) the dimers $\{(RC_5H_4)_2Y[C(H) = N\text{-}Bu\text{-}t]\}_2$ with bridging formimidoyl groups.[27]

The vibrational spectra methods of the complexes Cp_2LnBH_4. .THF (Ln = Sm, Er, or Yb), synthesised by the interaction of Cp_2LnCl with sodium tetrahydroborate, suggested[28] that, for Ln = Sm the anion is a tridentate ligand (C). When the Ln^{3+} cation is smaller (for example, when Ln = Yb) a complex with a bidentate tetrahydroborate group (D) is formed and the removal of coordinated THF by heating *in vacuo* gives polymeric structures, (E):



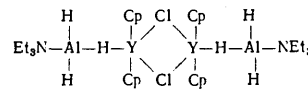
(C) (D) (E)

The complex $(Cp_2YCl)_2AlH_3.Et_2O$ has been obtained by the reaction of AlH_3 with dicyclopentadienylyttrium chloride.[29] Its investigation by X-ray diffraction showed that two of the three hydrogen atoms in the AlH_3 group are involved in the formation of the intermolecular Y–H–Al bridges, which leads to the formation of oligomeric chains containing the dimeric units $(Cp_2YCl)_2$:



The secondary Cl...Al bonds formed evidently make a significant contribution to the stability of the complex.

The same workers showed[30] that, when the ether in this complex is replaced by the more basic triethylamine, only one of the three hydrogen atoms in AlH_3 assumes the bridging position. As a result, the product of the reaction of $[Cp_2YCl]_2$ with $AlH_3.NEt_3$ is no longer a polymer but a dimer having the following structure:



The interaction of lithium tetrahydroaluminate with Cp_2YCl gives rise to the hydrides $(Cp_2YH)_2(AlH_3)_2$ containing bridging hydrogen atoms.[31]

III. COMPOUNDS WITH A LANTHANIDE–CARBON σ-BOND

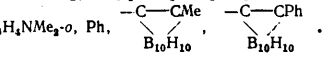
The following main types of lanthanide compounds containing σ-linked organic ligands are known:

$$R_3Ln,\ R_2LnX,\ RLnX_2,\ Li_x[LnR_{3+x}],\ Cp_2LnR,$$
$$Cp_2Ln(\mu\text{-}R)_2AlR_2,\ Cp_2Ln\langle^{CH_2}_{CH_2}\rangle PR_2,\ Cp_2Ln\langle^{R}_{CH_2-PR'_2}$$

A general and most convenient method of synthesis of complexes of the R_3Ln series involves reactions of alkyl- or aryl-lithium with the lanthanide trichlorides:[32–39]

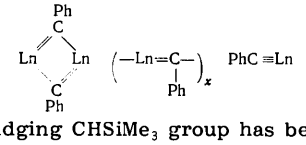
$$3RLi + LnCl_3 \xrightarrow{THF} R_3Ln + 3LiCl;$$

Ln = Sc, Y, La, Tb, Er, Tm, Yb, Lu; R = CH_2—Bu-t, CH_2SiMe_3, $CH_2(SiMe_3)_2$, $CH_2SiMe_2C_6H_4OMe$-*o*, $CH_2C_6H_4NMe_2$-*o*, Ph,

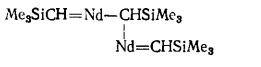


In most cases the products contain the coordinated solvent ($R_3Ln.2THF$). The formation of $Me_3La.THF$ has been noted,[32] but this compound has not been isolated in a pure state.

All the complexes R_3Ln decompose rapidly on contact with oxygen and moisture. Their thermal stability is determined by the nature of the substituent R. Alkyl derivatives decompose in the temperature range 50–100 °C. The compounds with R = CH_2SiMe are still less stable, decomposing slowly at room temperature.[37] Decomposition of the compound $(Me_3SiCH_2)_3Er.(THF)_2$ leads to the evolution of Me_4Si and the formation of the polymeric complex $[(Me_3SiCH)(Me_3SiCH_2)Er]_x$. Analogous results were obtained in a study of the reactions of YCl_3 and $NdCl_3$ with the alkyl-lithium reagents $LiCH_2Ph$, $LiCH_2C(Me)_2Ph$, and $LiCH_2SiMe_3$.[40–43] In the reaction with benzyl-lithium the formation of $(PhCH_2)_3Ln$ complexes in the initial stages has been postulated. These then decompose rapidly with evolution of toluene and the formation of compounds having the composition PhCLn. According to the authors of the above studies, the products can have the structures of carbene- or carbyne-metal complexes:



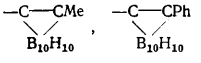
A dimer with a bridging $CHSiMe_3$ group has been proposed for the structure of the product of the reaction of $NdCl_3$ with $LiCH_2SiMe_3$.[42]



Derivatives of bivalent lanthanides of the type R_2Ln are known for europium and ytterbium. Most of them have been obtained by the oxidation reduction transmetallation reaction between R_2Hg and the metallic lanthanide:[44–49]

$$R_2Hg + Ln \rightarrow R_2Ln + Hg$$

Ln = Eu, Yb; R = C≡C—Bu-t, C≡CPh, C_6F_5, HC_6F_4-*p*,



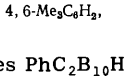
The acetylides $(RC \equiv C)_2Ln$ can be synthesised in addition by the direct interaction of the substituted acetylene RC ≡ CH with the metallic lanthanide in liquid ammonia[50] or by the reaction of phenylacetylene with R_2Yb (R = C_6F_5 or C ≡ C–Bu-t).[49]

The phenylethynyl and carbaboranyl complexes decompose on heating above 200 °C. The polyfluorophenyl derivatives are less stable and decompose at an appreciable rate even at room temperature. Judging from the conditions and products of the reactions of R_2Yb (R = C_6F_5, *p*-HC_6F_4, or C ≡ CPh) with aldehydes, ketones,[51] Ph_3SnCl, $HgCl_2$, I_2, C_6F_5COOH, and certain nickel, rhodium, and platinum complexes,[52] the reactivity of R_2Ln is similar to that of the organolithium and organomagnesium compounds.

The ease of their reactions with alkyl or aryl-iodides is extremely characteristic of the lanthanides. In most cases this results in the formation of a mixture of R_3Ln, R_2LnI, $RLnI_2$, and LnI_3, which are difficult to separate. However, under these conditions, samarium, europium, and ytterbium give rise to the compounds RLnI, whose properties are close to those of Grignard reagents:[53,54]

$$RI + Ln \xrightarrow{THF} RLnI$$

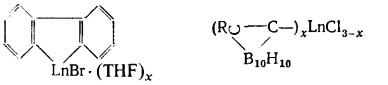
Ln = Sm, Eu, Yb; R = Me, Et, Ph, *o*-MeC_6H_4, 2.6-$Me_2C_6H_3$, 2, 4, 6-$Me_3C_6H_2$,



The carbaboranyl derivatives $PhC_2B_{10}H_{10}LnI$ (where Ln = Sm, Eu, or Yb) have been obtained in addition by the reaction of phenylcarbaboranyl-lithium with LnI_2.[54]

The compounds RLnI are in many respects similar to organomagnesium derivatives, but significant differences have been observed in their reactivities, particularly in the interaction with carbonyl compounds[55–58] and unsaturated hydrocarbons.[59,60]

It has been noted[57] that praeseodymium, neodymium, gadolinium, and dysprosium react with iodoethane to form coloured solutions containing EtLnI complexes but evidence for their structure is not quoted. On the other hand, a study of the reactions of Ph_3CCl, $PhCH_2Cl$, and PhBr with metallic praeseodymium, neodymium, gadolinium, and holmium established[61–63] that these reactions lead to the formation of compounds of tervalent lanthanides $RLnX_2$. The latter decompose slowly at room temperature, producing more complex organolanthanides and products of the reactions of the radicals R. The lanthanum complex $Ph_3CLaCl_2.N(CH_2CH_2OCH_2.CH_2OCH_2CH_2)_3N$ has been obtained by the reaction of triphenylmethyl-lithium with $LaCl_3.L$.[64] The interaction of 2,2′-dilithiobiphenyl and carbaboranyl-lithium with $Ln(Hal)_3$ also leads to the formation of the corresponding derivative of a mixed type:



Ln = Pr, Sm, Ho, Yb (Ref.65) Ln = La, Tm; R = Me, Ph
x = 1, 2 (Ref.39)

In those cases where the molar ratio of the reactants in the reactions of RLi with $Ln(Hal)_3$ described above exceeds 3, the products are bimetallic complexes of the *ate*-type:

$$LnCl_3 + (3 + x)\,RLi \rightarrow Li_x[LnR_{3+x}] + 3LiCl.$$

The phenyl derivatives $Li[LnPh_4]$ (Ln = La or Pr) have been isolated in a form free from the solvent.[32] All the remaining complexes contain electron-donating ligands [THF, tetramethylethylenediamine (TMED), and ether]: $[Li(THF)_4].[LnR_4]$ (Ln = Y, Sm, Er, Tb, Yb, or Lu; R = 2,6-$Me_2C_6H_3$, t-Bu, or CH_2SiMe_3,[38,66,67] $[Li(THF)_4][LnClR_3]$ [Ln = Er or Yb; R = $CH(SiMe_3)_2$,[38] $[Li(TMED)_2][LnR_4]$ (Ln = Y, Er, Yb, or Lu; R = t-Bu or CH_2SiMe_3),[36,68] $[Li(TMED)_3][LnMe_6]$ (Ln = Y or La–Lu).[68,69]

Bimetallic compounds with bulky carbaboranyl substituents $(MeC_2B_{10}H_{10})_3Yb.THF.MeC_2B_{10}H_{10}Li.(THF)_2$ and $Me_2C_2B_{10}H_{10}YbCl_2.MeC_2B_{10}H_{10}Li.2THF$[39] apparently also have the structure of *ate*-complexes.

The alkynyl complexes $[Li(THF)_4][Ln(C \equiv C\text{-Bu-t})_4]$ (Ln = Sm, Er, or Lu) are formed when isobutane is displaced from $[Li(THF)_4][Ln(t\text{-Bu})_4]$ by t-butylacetylene.[70] X-Ray diffraction study of $[Li(THF)_4][Lu(2,6\text{-}Me_2C_6H_3)_4]$ [66] and $[Li(THF)_4]\{Yb[CH(SiMe_3)_2]_3Cl\}$ [38] showed that the lanthanide atoms in these compounds are tetrahedrally coordinated, while those in $[Li(TMED)_3][LnMe_6]$ (Ln = Ho or Er)[68] are octahedrally coordinated.

All the bimetallic complexes rapidly decompose in air but are fairly stable, with the exception of the etherate $[Li(Et_2O)_4][Lu(CH_2SiMe_3)_4]$, in an inert atmosphere or *in vacuo*.

A large group of compounds containing a wide variety of σ-linked ligands is formed by cyclopentadienyl derivatives of the type Cp_2LnR. They are usually synthesised by the reaction of RLi with the corresponding chloride:

$$Cp_2LnCl + RLi \xrightarrow{THF} Cp_2LnR\cdot THF + LiCl\ ;$$

Ln = Y, Dy, Ho, Er, Yb; R = Me [71—73]; Ln = Gd, Er, Yb, Lu; R = Me, Et, iso-Pr, Bu, t-Bu, t-C_6H_{11}, CH_2SiMe_3, CH_2Ph, Ph_3C, 4-ClC_6H_4, 4-MeC_6H_4 (Refs.74, 75); Ln = Gd, Yb; R = (Ref.71); Ln = Sc, Gd, Ho, Er, Yb; R = C ≡ CPh (Refs.71, 76).

The ethynyl derivatives are also obtained by substituting the methyl group in Cp_2LnMe [70] or one Cp group in Cp_3Ln [77] by acetylenes:

$$Cp_2LnR + HC{\equiv}CR' \rightarrow Cp_2LnC{\equiv}CR' + RH\ ;$$

Ln = Nd, Er, Yb; R = Me, η⁵-Cp, R'=Bu, C_6H_{11}, Ph, ferrocenyl.

Using the same reactions, complexes with methylcyclopentadienyl rings have been synthesised:

$(Me_5C_5)_2LnMe\cdot Et_2O$ (Ln=Yb, Lu) (Ref.78),

$(Me_5C_5)_2YbMe\cdot THF$, $[(Me_5C_5)_2YbMe_2]Lu\times$

$\times(Et_2O)_2$, $[(Me_5C_5)_2YbClMe]Li\cdot(Et_2O)_2$ (Ref.79),

$(MeC_6H_4)_2SmC{\equiv}C-Bu\text{-}t$ (Ref.80),

[1, 1'—$(CH_2)_3(C_5H_4)_2$] $LnC{\equiv}CPh$ (Ln=La, Ce) (Ref.81).

Depending on the nature of R and the isolation method, the complexes can contain solvent or can be non-solvated. In the majority of the complexes the substituents R are of the bridging type, which is the reason for the dimeric form of these compounds. X-Ray diffraction of the complexes $Cp_2LnBu\text{-}t.THF$,[82] $Cp_2LuCH_2SiMe_3.THF$, and $Cp_2LuC_6H_4Me\text{-}4$ [74] has shown that in the presence of bulky substituents the compounds are monomeric.

The study of the reactivity of these complexes in relation to $(Me_5C_5)_2LnMe$ (Ln = Y or Lu) has shown recently[83,84] that a methyl group linked to the metal is readily displaced not only by acetylenes but also by hydrocarbons without activated C—H bonds:

$$(Me_5C_5)_2LnMe + RH \rightarrow (Me_5C_5)_2LnR + MeH\ ;$$

R = Me, Et, Pr, Ph, CH_2SiMe_3, C_5H_4N.

On interaction with diphenylacetylene, the bivalent lanthanide derivative $(Me_5C_5)_2Sm$ gives rise to the adduct $(Me_5C_5)_2Sm(Ph)C \equiv C(Ph)Sm(C_5Me_5)_2$.[25]

σ-Complexes with Ln^{4+} are known for cerium: Cp_3CeR, $(Ind)_2CeR_2$ (Ind = indenyl; R = Me, Et, Ph, CH_2Ph or COPh).[85]

The first cyclo-octetetraenyl complexes with σ-linked ligands, namely $(C_8H_8)Lu(CH_2SiMe_3).(THF)_2$ and $(C_8H_8)Lu.(C_6H_4CH_2NMe_2\text{-}o).THF$ have been obtained recently by the reaction of RLi with the chloride $(C_8H_8)LuCl.THF$.[86]

The bimetallic lanthanide derivatives $Cp_2Ln(R)_2AlR_2$ with bridging alkyl groups are formed in the reaction of cyclopentadienyl-lanthanide chlorides with lithium tetra-alkylaluminates:[72,87,88]

$$Cp_2LnCl + LiAlR_4 \rightarrow Cp_2Ln(R)_2AlR_2 + LiCl\ ;$$

R = Me, Et.

The presence of bridging alkyl groups has been confirmed by X-ray diffraction of the ytterbium compound $Cp_2Yb(\mu\text{-}Me_2).AlMe_2$.[88]

The zwitter-ionic lanthanide complexes $Ln[(CH_2)_2PR_2]_3$ (Ln = La, Pr, Nd, Sm, Gd, Ho, Er, or Lu; R = Me or t-Bu),[89,90] $Cp_2Lu(Cl)CH_2PPh_3$,[90] $Cp_2Lu(R)CH_2PPh_3$ (R = t-Bu or CH_2SiMe_3), and $Cp_2Lu(Bu\text{-}t)CH(SiMe_3)PMe_3$ [91] have been obtained by the reactions of the ylides CH_2PR_3 with the lanthanide chloride derivatives $LnCl_3$ and Cp_2LnCl.

IV. π-COMPLEXES OF ORGANOLANTHANIDES

1. Complexes with Alkenes and Alkynes

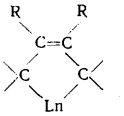
Like the compounds of *d*-metals, the lanthanide derivatives are capable of forming stable π-complexes with alkenes and alkynes. Allyl derivatives of samarium, holmium, and erbium have been obtained by the Girgnard reaction:[92]

$$Cp_2LnCl + C_3H_5MgBr \xrightarrow[-78^\circ]{} Cp_2LnC_3H_5 + MgBrCl\ .$$

The scandium complex $Cp_2ScC_3H_5$ had been synthesised earlier by the same method.[76]

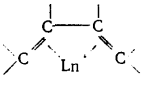
The allyl complexes are readily oxidisable and hydrolysable. Their infrared spectra contain an absorption band at 1533 cm^{-1}, which is characteristic of the delocalised C—C bonds in the allyl fragment.

The cocondensation of the lanthanide and buta-1,3-diene of 2,3-dimethylbuta-1,3-diene at −196 °C yielded the solids $Ln(C_4H_6)_3$ and $Ln(Me_2C_2H_4)_2$ (Ln = La, Sm, or Er),[93] which decompose in air. Their structure has not been accurately established. Judging from the hydrolysis products, among which the main one is but-2-ene, the compounds contain dialkyl groups:



R = H, Me.

However, in this case one can assume that the metal in the complexes is in the +4 oxidation state for LnR_2 and +6 for LnR_3, which appears unlikely. As an alternative, the authors propose a π-dienyl group with a formally zerovalent metal:



Apparently complexes of an analogous kind are formed in the cocondensation of the lanthanide metal vapours with disubstituted acetylenes RC ≡ CR.[94] The high molecular weights of the complexes indicate their oligomeric structure.

More definite structural data have been obtained for the 2,4-dimethylpentadienylneodymium complex $(C_7H_{11})_3Nd$, synthesised by the reaction of $NdCl_3$ with the 2,4-dimethylpentadienyl anion.[95] According to XRD data, the neodymium atom is surrounded by three dienyl groups. The atoms of the pentadienyl chain have a nearly planar disposition. The lengths of the Nd—C[1(5)] [2.801(9)Å] and Nd—C(3) [2.749(10) Å] bonds are reduced compared with those of the Nd—C[2(4)] [2.855(8) Å] bonds, which reflects the difference between the charge densities on the carbon atoms in the different positions and indicates a significantly ionic nature of the metal—carbon bond.

2. Cyclopentadienyl Derivatives

Compounds with cyclopentadienyl substituents are the most thoroughly investigated organic derivatives of the lanthanides. The following main groups of complexes are known at the present time: Cp_2Ln (Ln = Sm, Eu, or Yb); Cp_3Ln (Ln = La—Lu); Cp_4Ce, Cp_3CeX, and Cp_2CeX_2; Cp_2LnX, $CpLnX_2$,

$(Cp_2LnX_2)M$, Cp_2LnR, and $(Cp_2LnR_2)M$ (Ln = La–Lu; M = Li or Al). The last two groups contain an Ln–C σ-bond and were examined above in Section III.

The most general method of synthesis of the cyclopentadienyl compounds, including Cp_4Ce, involves the interaction of alkali metal or magnesium cyclopentadienides with the salts LnX_3:[96–98]

$$LnX_3 + 3CpM \rightarrow Cp_3Ln + 3MX;$$
$$(PyH)_2[CeCl_6] + 4CpNa \rightarrow Cp_4Ce + 4NaCl + 2(PyH)Cl.$$

However, one should note that the possibility of synthesising Cp_4Ce by the above reaction has been denied by Deacon et al.[99] and it has been shown that this pathway leads to Cp_3Ce. Doubt has also been cast on studies on the synthesis of Cp_3CeX and fluorenyl and cycloheptatrienyl derivatives of cerium(IV).[99]

Tricyclopentadienylpromethium has been obtained using Cp_2Be as the donor of Cp groups.[100]

The products contain as a rule molecules of the electron-donating solvent, in which these reactions are carried out, coordinated to the lanthanide atom. Complexes free from the solvents are obtained when the products are sublimed or heated cautiously *in vacuo* (Ln = Eu)[101] and also when the syntheses are carried out in benzene or ether.

Complexes with a bivalent Ln atom have been obtained in the case of europium and ytterbium by the reaction of cyclopentadiene with the corresponding metal in liquid ammonia[102] and by the reduction of Cp_2LnCl to Cp_2Ln with sodium or ytterbium in THF.[103]

A method has been proposed for the synthesis of the cyclopentadienyl complexes of the lanthanides based on the oxidation-reduction transmetallation reaction between Cp_2Hg and the lanthanides.[104–106] Depending on the reactant ratio and the nature of the lanthanide, Ln^{2+} and Ln^{3+} derivatives can be obtained in 30–60% yield:

$$Cp_2Hg + mLn \xrightarrow{THF} (m-1)\,Ln/Hg + Cp_2Ln\cdot(THF)_x;$$
$$Ln = Sm,\ Eu,\ Yb;\ m = 4,\ 5;\ x = 2–4;$$
$$3Cp_2Hg + 2Ln \rightarrow 3Hg + 2Cp_3Ln\cdot(THF)_x.$$

The reaction of metallic lanthanides with cyclopentadienylthallium is more convenient from the preparative standpoint:[107]

$$x\,CpTl + Ln \rightarrow Cp_xLn + xTl;$$
$$Ln = Nd,\ Sm\ (x = 3);\ Ln = Yb\ (x = 2,\ 3).$$

The authors of the same study showed that the synthesis of Cp_2Yb involved the initial formation of Cp_3Yb, but Yb^{3+} is rapidly reduced further to Yb^{2+}.

The first soluble bivalent samarium complex $(Me_5C_5)_2Sm.(THF)_2$ has been obtained by the cocondensation of the metal and ligand vapours at −120 °C.[108]

All the cyclopentadienyl derivatives of lanthanides, including halogenoderivatives and bimetallic complexes, are solids (m.p. 250–400 °C) and are extremely sensitive to moisture and oxygen (only the Ce^{4+} complexes are stable). On heating *in vacuo*, they sublime (with the exception of Cp_3Eu, which decomposes, and the involatile bimetallic compounds) in the temperature range 150–250 °C and at a pressure of 10^{-3} mmHg. The unsubstituted Cp_3Ln are sparingly soluble in alkanes and aromatic hydrocarbons but are readily soluble in THF, pyridine, and other electron-donating solvents. The introduction of alkyl groups into the Cp rings increases the volatility and solubility of the complexes. The structures of more than 20 compounds of this series have now been investigated: $(Cp_3Pr)_n$,[109] $(Cp_3Sm)_n$,[110] $(Cp_3Sc)_2$,[111] $[(MeC_5H_4)_3Nd]_4$,[112] $Cp_3Pr.CNC_6H_{11}$,[113] $Cp_3Gd.THF$,[96] $(Cp_3Yb)_2.NC_4H_4N$,[114] $(Me_3C_5)_2Sm.(THF)_2$,[108] $(Me_5C_5)_2Yb.(C_5H_5N)_2$,[115] $(MeC_5H_4)_2Yb.THF$,[116] $(Me_5C_5)_2Yb.THF.(PhMe)_{1/2}$,[117] $(Me_3SiC_5H_4)_2Yb.(THF)_2$,[118] and $Cp_2Yb.DME$ [119] [the complexes Cp_2LnCl and $(Cp_2LnCl_2)M$, whose structures have been investigated are considered below].

X-Ray diffraction, vibrational, electronic spectroscopic data, and measurements of magnetic susceptibility have shown that the bond between the cyclopentadienyl rings and the lanthanide atom is ionic.[7,120,121] The most characteristic chemical property of the compounds Cp_xLn (x = 2 or 3), apart from their hydrolytic and oxidative instability, is a very marked tendency towards the formation of complexes of the type $Cp_3Ln.L$ with Lewis acids, for example, with NH_3, THF, DME, R_3P, etc.[7,115,122,123] Less basic ligands are then displaced by more basic ones.

It is of interest that $Me_2PCH_2PMe_2$ is a monodentate ligand in the complex $(MeC_5H_4)_2YbCl.Me_2PCH_2PME_2$, in contrast to the bidentate ligand $Me_2PCH_2CH_2PMe_2$ in the coordination polymer $[(MeC_6H_4)_2Yb.Me_2PCH_2CH_2PMe_2]_n$.[124] The CO and NO groups of the nitrosyl carbonyl complexes of transition metal derivatives of the type $[(MeC_5H_4)Mn(CO)NO]_2$ and $Me_2Sn[Mn(CO)_5]_2$ can also play the role of electron donors.[125–127] The adducts formed under these conditions have been investigated by infrared spectroscopy and NMR.

The cyclopentadienyl rings in Cp_3Ln are readily split off in reactions with proton-containing reagents (HCl, HCN)[16,123] and metal salts ($FeCl_3$, $LnCl_3$),[7,16] which leads to derivatives of the type Cp_2LnX. Fragmentation of the Cp derivatives of the lanthanides under electron impact begins with the elimination of the Cp ring.[3,128] The energy of the bond between the Ln^{3+} cation and the cyclopentadienyl rings is in the range 45–78 kcal mol^{-1}.[128,129]

Complexes of the type Cp_2LnX are readily obtained also in the reactions of $LnCl_3$ with alkali metal[16] or thallium[28] cyclopentadienides (in proportions of 1 : 2). Among them lanthanum, cerium, and praseodymium derivatives were missing for a long time. However, the use of trimethylene-1,1-bis-cyclopentadienyl or Me_3Si-substituted Cp rings as ligands made it possible to obtain halogen-containing complexes of these metals as well.[81,97] The same methods, i.e. the reactions of Cp_3Ln with LnCl and HCl or $LnCl_3$ with CpNa, are used to synthesise the monocyclopentadienyl compounds $CpLnCl_2$.[130] Dicyclopentadienylmercury can also serve as a donor of Cp groups.[106]

In terms of their physical properties, the halogeno-derivatives are close to the compounds of the Cp_3Ln series. Their reactivity is determined by the presence of a mobile anion X, which can be readily replaced by another functional group by reaction with the corresponding alkali metal derivative:

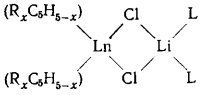
$$Cp_2LnX + M\text{-}Z \rightarrow Cp_2Ln\text{-}Z + MX;$$
$$M = Li,\ Na;\ Z = Alk,\ OR,\ OCOR,\ NH_2,\ PR_2.$$

These reactions are examined in detail in other Sections of this review. The complexes Cp_3CeCl and Cp_2CeCl_2 [synthesised by the reactions of $(PyH)_2CeCl_6$ with CpNa][7] and their derivatives Cp_3CeZ,[131,132] obtained like the complexes Cp_2LnZ, are known for cerium.

In recent years attention has been concentrated in the study of derivatives of Cp_2LnX series (as well as other cyclopentadienyl complexes of the lanthanides) on the determination of their structure by X-ray diffraction. It was found that the metal atoms in the $CpErCl_2.(THF)_2$,[133] $(Me_5C_5)_2.YbSCSNEt_2$,[134] $(MeC_5H_4)_2YbCl.Me_2PCH_2PMe_2$,[124] and $\{[(Me_3Si)_2C_5H_3]_2LnCl\}_2$ (Ln = Sc, Pr, or Yb)[97] have distorted tetrahedral coordination, as in the dimers $[(MeC_5H_4)_2YbCl]_2$ [135] and $(Cp_2ScCl)_2$ [136] investigated previously.

A distinctive feature of the cyclopentadienyl complexes of the lanthanides is their tendency to form bimetallic complexes of the type $[Cp_2LnCl_2]Li.(THF)_2$.[16,97,137–139] These compounds are apparently formed in the intermediate stages of all the reactions of $LnCl_3$ with alkali metal cyclopentadienides.

For the 1 : 2 reactant ratio, they become the final products and can be isolated in high yields. X-Ray diffraction studies of the complexes $\{[(Me_3Si)_2C_5H_3]_2NdCl_2\}Li.(THF)_2$,[122] $[(Me_5C_5)_2YbCl_2]Li.(Et_2O)_2$,[139] and $[(Ph_2MeSiC_5H_4)_2.YbCl_2]Li.(Et_2O)_2$ [139] showed that the Ln and Li atoms in them are linked by bridging Cl atoms:



The iodine analogue $[(Me_5C_5)_2YbI_2]Li.(Et_2O)_2$ and the aluminium-containing complex $[(Me_5C_5)_2YbCl_2]AlCl_2$ have the same structure.[139] The solvents L in these complexes are usually THF or Et_2O, in which the syntheses were carried out. These solvent molecules can also be readily substituted by other stronger bases, for example DME [dimethoxyethane (Editor of Translation)] and tetramethylethylenediamine.

A different structure, characterised by the presence of the anion $[(Me_3SiC_5H_4)_2NdCl_2]^-$, has been proposed for the complex $[(Me_3SiC_5H_4)_2NdCl_2][Li(THF)_4]$ formed when $[(Me_3SiC_5H_4)_2NdCl]_2$ reacts with $LiCl.(THF)_4$ or when $Me_3SiC_5H_4Li$ reacts with $NdCl_3$.[140] The authors found evidence supporting this structure, namely the fact that the Cl–Nd–Cl angle (99.3°), the Nd–Cl distance [2.668(4) Å], and the average Nd–C_{ring} distance (2.78 Å) in the complex $[(Me_3SiC_5H_4)_2][AsPh_4]$ differ appreciably from the corresponding values (81.1°, 2.744 Å, and 2.76 Å) in the bridged compound $[(Me_3Si)_2C_5H_3]_2Nd(\mu\text{-}Cl)_2Li.(THF)_2$.

The reaction of equimolar amounts of $YbCl_3$ and Me_5C_5Li yielded the monocyclopentadienyl complex $[Me_5C_5YbCl_3]Li.THF$.[139] The analogous iodine derivative $(Me_5C_5YbI_3)Li.(Et_2O)_2$ has been obtained by the reaction of metallic ytterbium with Me_5C_5I in the presence of LiI.[79]

3. Indenyl, Fluorenyl, and Cycloheptatrienyl Complexes

A study of the idenyl complexes of the lanthanides was first undertaken by Tsutsui and Gyfling in their search for evidence that *f* electrons are involved in the formation of chemical bonds.[141,142] The compounds $(C_9H_7)_3Ln.THF$ (Ln = La, Sm, Gd, Tb, Dy, or Yb) were obtained by the reaction of C_9H_7Na with $LnCl_3$ in THF. On the basis of NMR data, it was postulated that the samarium complex is covalent. However, subsequent X-ray diffraction study of a non-solvated $(C_9H_7)_3Sm$ specimen demonstrated the η^5-coordination of the indenyl ligands.[143]

The cerium derivatives $(C_9H_7)_xCeCl_{4-x}$ (x = 2, 4)[22,98] and the tetrahydroindenyl complexes $(C_9H_{11})_xLnCl_{3-x}$ (Ln = La, Nd, or Er; x = 1, 2)[144] were synthesised analogously.

The properties of the indenyl complexes are similar to those of the cyclopentadienyl compounds, but, in contrast to the latter, they do not sublime and are soluble in hydrocarbons.

Among the series of fluorenyl derivatives, tri- and tetrafluorenylcerium, synthesised by the reaction of fluorenylsodium with $(PyH)_2CeCl_6$,[145] and the bimetallic complexes $(C_{13}H_9)_2LnCl_2Li.(THF)_2$ (Ln = La, Nd, Sm, Ho, or Lu) are known.[146,147] The latter are formed by the reaction of $C_{13}H_9Li$ with the chlorides $LnCl_3$. Analysis of the infrared and ^1H NMR spectra of these complexes indicated that the fluorenyl residues are linked via σ-bonds to the Ln atom, while the chlorine atoms are bridging; the THF molecules are coordinated to the lithium atom.

It has been shown[148] that the addition of UCl_4 to lithium R-cycloheptadienide induces the rapid formation of an unstable organouranium compound containing the cycloheptatrienyl anion $C_7H_6R^-$ (R = H, Me, or Bu) as the ligand. Analogous complexes have been obtained with gadolinium and erbium chlorides. It has been suggested that the ions of the *f* elements attract to themselves the electron density of the cycloheptadienyl ligands, increasing thereby the polarisation of the C–H bonds of the methylene groups and hence facilitating the elimination of the proton and the formation of trienyl ligands.

The cerium complex $(C_7H_7)_2CeCl_2$ has been obtained in the form of brown crystals by the reaction[149]

$$(PyH)_2CeCl_6 + 2C_7H_8 \rightarrow (C_7H_7)_2CeCl_2 + 2C_5H_5N\cdot HCl + 2HCl\,.$$

Its structure has been confirmed by elemental analysis and infrared spectroscopic data.

4. Cyclo-octatetraenyl Complexes

During the last five years, these compounds have not been investigated; after the establishment of their similarity to the thoroughly investigated "uranocene", the interest in them decreased appreciably. The lanthanide compounds containing the $C_8H_8^{2-}$ dianion can be obtained by the reaction of the metal with cyclo-octatetraene in liquid ammonia:[150]

$$Ln + C_8H_8 \rightarrow LnC_8H_8\,;$$
$$Ln = Eu,\ Yb\,.$$

In a more universal method, $K_2C_8H_8$ is used:[151,152]

$$LnCl_3 + xK_2C_8H_8 \xrightarrow{THF} \begin{cases} \rightarrow [(C_8H_8)_2Ln]K + 3KCl\,; \\ \quad Ln = Sc,\ Y,\ La,\ Ce,\ Pr,\ Nd,\ Sm,\ Gd,\ Tb\,. \\ \rightarrow [C_8H_8LnCl\cdot(THF)_2]_2 + 2KCl\,; \\ \quad Ln = Sc,\ Ce,\ Pr,\ Nd,\ Sm\,. \end{cases}$$

In the latter case, bimetallic or chlorine-containing complexes are formed, depending on the ratio of the initial reactants. It has been shown by X-ray diffraction[153] that the cerium and bridging chlorine atoms in the cerium dimer $[C_8H_8CeCl.(THF)_2]_2$ form a planar four-membered ring with Ce–Cl distances of 2.855(2) and 2.935(2) Å. The cerium atom is located symmetrically relative to the C_8H_8 planar ring. The anion $(C_8H_8)_2Ce^-$ in the complex $[(C_8H_8)_2Ce][K(MeOCH_2CH_2)_2O]$ has the characteristic "metallocene" structure with an average Ce–C distance of 2.742(8) Å.[154]

The complex $(C_8H_8)_2Ce$ has been isolated in the form of a black crystalline substance on reduction of tetraisopropoxycerium with triethylaluminium in the presence of cyclo-octatetraene.[155] A decrease of the excess of C_8H_8 leads to the formation of the complex $(C_8H_8)_3Ce_2$, in which there are two different types of C_8H_8 ligands according to infrared spectroscopic data. Products with the same stoichiometry have been obtained by the cocondensation of the lanthanide (Ln = La, Ce, Nd, or Er) and cyclo-octatetraene vapours at −196 °C.[156,157] It has been shown by X-ray diffraction of the neodymium derivative $[(C_8H_8Nd.(THF)_2][(C_8H_8)_2Nd]$ [157] that the C_8H_8 rings in the anion $(C_8H_8)_2Nd^-$ are not parallel and are separated by different distances from the Nd atom. The cation $[C_8H_8Nd.(THF)_2]^+$ is located asymmetrically relative to the anionic group and two carbon atoms of one of the C_8H_8 rings of the anion are in the coordination sphere of the cationic Nd atom (see Figure). The corresponding lanthanum, cerium, and erbium complexes are isostructural with the neodymium complex.

Quantum-chemical calculation for the anion $(C_8H_8)_2Ce^-$ showed[158] that the interaction of the 5*d* orbitals of the metal with the ligands makes a decisive energy contribution, while the *f* electron is localised at the metal.

The cyclopentadienyl-cyclo-octatetraenyl complexes C_8H_8LnCp are known for Sc, Y, Nd, Sm, Ho, and Er.[151,159] A "sandwich" structure has been proposed for these compounds.

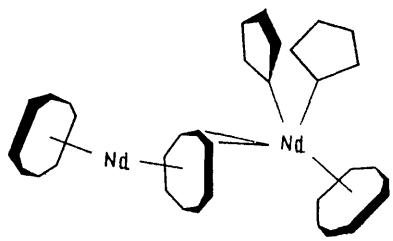
V. COMPOUNDS WITH AN Ln–E BOND

1. Compounds with an Ln–N Bond

The amido-derivatives $Ln(NR_2)_x$ (x = 2, 3), $Cl_2Ln\,NR_2$, and Cp_2LnNR_2, the phthalocyanines Pc_2Ln and PcLnH, and porphyrins are known among complexes of this class. In all cases R in the NR_2 fragment is the trimethylsilyl group. Only a mention has been made of the isopropylamides $Ln[N(Pr\text{-}iso)_2]_3$ (Ln = Y, Yb, or Nd)[160] without any description of the methods of synthesis and properties of these compounds. The amidolanthanides, obtained for the first time in 1972[161] by the reaction

$$LnCl_3 + 3LiN(SiMe_3)_2 \rightarrow Ln[N(SiMe_3)_2]_3 + 3LiCl$$

have been most thoroughly investigated.



The structure of the complex $[C_8H_8Nd(THF)_2][(C_8H_8)_2Nd]$.

Derivatives of bivalent ytterbium and europium are formed when EuI_2 and YbI_2 are used in this process[162] and also when the chloride $ClEu(NR_2)_2$ is reduced with sodionaphthalene.[163]

The disproportionation reaction[164]

$$2\,PrCl_3 + Pr[N(SiMe_3)_2]_3 \rightarrow 3Cl_2PrN(SiMe_3)_2$$

which is extremely characteristic of lanthanide compounds, has been used to synthesise mixed chloroamide complexes. The same product and its neodymium analogue have been obtained by the hydrochlorination of $Ln[N(SiMe_3)_2]_3$.[164]

An X-ray diffraction study has been made of the complexes $Ln[N(SiMe_3)_2]_3$ (Ln = Nd,[165] Sc, Eu, or Yb[166]), $Eu[N(SiMe_3)_2]_2(DME)_2$,[163] and $Yb[N(SiMe_3)_2]_2[Me_2PCH_2CH_2.PMe_2]$[162] and showed that, in the absence of a coordinating ligand, the group $Ln(N<)_3$ has a pyramidal configuration (the Ln atom is displaced from the N_3 plane by approximately 0.4 Å). The addition of the ligand (DME) increases the polarity of the $Ln(N<)_3$ fragment.

In the last of the complexes enumerated above interaction between the Yb atom and the carbon atoms of the $SiMe_3$ groups, which is unusual for a compound of this kind, was observed. (The Yb...C distance is 3.4 Å, which is less than the sum of the covalent radius of Yb^{2+} and the van der Waals radius of the methyl group.)

Compounds with the NH_2 group at the lanthanide atom, namely $CpLnNH_2$ (Ln = Er or Yb) have been synthesised in the course of a study of the reactivity of the cyclopentadienyl derivatives. They are formed when Cp_2LnCl interacts with sodium amide[167] and in the thermolysis of the ammine complexes Cp_3LnNH_3.[168] The last reaction has also been used to synthesise the cyclopentadienylbis(trimethylsily)amide complexes $(Me_5C_5)_2LnN(SiMe_3)_2$ and $Me_5C_5Ln[N(SiMe_3)_2]_2$ (Ln = Nd or Yb).[137]

The lanthanide amides $Ln(NR_2)_3$ are crystalline substances, which are extremely sensitive to moisture and which sublime *in vacuo* at 80–100 °C. The cyclopentadienyl derivatives Cp_2LnNR_2 are less volatile. Their high reactivity and relative availability makes these compounds convenient starting materials for the synthesis of organolanthanides of other classes. Thus it has been found that $Ln[N(SiMe_3)_2]_3$ (Ln = Pr or Nd) react exothermically with carbon dioxide in DME at 20 °C and 1 atm, forming the complexes $Ln[N(SiMe_3)_2]_3.2CO_2$.[169] Their structure has not been accurately established, but, on the basis of infrared spectroscopic data, one may conclude that it differs from that of the erbium and ytterbium carbamate complexes $Ln(OCONR_2)$, obtained by the reaction of LnX_3 with carbon dioxide and amines R_2NH.[170]

The phthalocyanine and porphyrin complexes of metals constitute a specific group of coordination compounds and are usually not dealt with in reviews and monographs devoted to the chemistry of organometallic compounds. We thought it useful to consider these compounds briefly, because they possess a number of interesting properties and information about them significantly completes our ideas about the possibilities of organolanthanides.

The complexes Pc_2LnH ($Pc = C_{32}H_{16}N_8^{2-}$), obtained by the reaction of lanthanide acetates with *o*-phthalonitrile at 280–290 °C, should probably be regarded as the first reliably characterised lanthanide-phthalocyanines.[171,172] This method is virtually the only convenient procedure for the synthesis of phthalocyanine compounds, which can have the compositions Pc_2LnX, Pc_2Ln, and Pc_3Ln_2. They are all intensely coloured crystalline substances which are stable in air. The interest in them has increased particularly after the discovery of the electrochemical properties of lanthanide-diphthalocyanines.[173] It has been established[174] that their colour is determined by the oxidation state of the lanthanide in the complex: violet for Pc_2Lu^{2-}, blue for $PcLu^-$, green for Pc_2Lu, and red-brown for Pc_2Lu^+.

An X-ray diffraction study of Pc_2NdH[175] showed that the neodymium atom in this complex occupies the central position between two parallel phthalocyanine ligands, one of which has the form of a saucer extended towards the Nd atom. One ligand has been rotated relative to the other by 45° around the normal to their planes. The Nd–N distance varies from 2.39 to 2.49 Å. The photoelectron spectrum of this complex[175] indicates the chemical equivalence of all eight central nitrogen atoms, whence it follows that the mobile hydrogen atom does not form a strong bond with any of them, although a weak interaction is not excluded.

A porphyrin complex, tetraphenylporphyrinacetylacetonato-europium, has been obtained (for use as a shift reagent) by heating $(C_5H_7O_2)_3Eu$ with tetraphenylporphyrin.[176] The compound is readily soluble in organic solvents and is stable in relation to oxygen and water. The samarium, gadolinium, erbium, and ytterbium complexes as well as the octaethylporphyrin complexes of europium, gadolinium, ytterbium, and lutetium have been obtained analogously.[177] The single band in the photoelectron spectra of the nitrogen atoms in these compounds indicates their equivalence. The relatively high energy of this band (398 eV) indicates a significantly covalent character of the Ln–N bond, according to the authors.[177]

2. Compounds with an Ln–P Bond

Apart from the complexes containing a P–Ln coordinate bond (which are considered among cyclopentadienyl derivatives), only a few compounds with the Ln–P group are known. They include the trisphosphine compounds

$Ln[P(Bu\text{-}t)_2]_3.(THF)_2$ (Ln = Y, Ho, Er, Tm, Yb, or Lu)[178] and derivatives of the Cp_2LnPR_2 series (Ln = Tb, Ho, or Er and R = t-Bu;[179] Ln = Yb and R = cyclo-C_6H_{11} [180]). Compounds of both types have been obtained by the reaction of $LiPR_2$ with the corresponding lanthanide chloride:

$$LnCl_3 + 3LiP(Bu\text{-}t)_2 \xrightarrow{THF} Ln[P(Bu\text{-}t)_2]_3.(THF)_2 + 3LiCl;$$
$$Cp_2LnCl + LiPR_2 \rightarrow Cp_2LnPR_2 + LiCl .$$

The exchange reaction between Cp_2ErCl and $Me_3SiP(Bu\text{-}t)_2$ has been used to obtain $Cp_2ErP(Bu\text{-}t)_2$.[175] When the tris-phosphine complexes are heated *in vacuo*, they lose the solvate THF and are converted into the coordination polymer $\{Ln[P(Bu\text{-}t)_2]_3\}_x$.

Bis(methylcyclopentadienyl)(diphenylphosphine)samarium was synthesised recently by the hydride method:[80]

$$[(MeC_5H_4)_2SmC{\equiv}CPh]_2 + 2HPPh_2 \rightarrow 2(MeC_5H_4)_2SmPPh_2 + 2PhCCH .$$

This reaction is particularly convenient for the formation of the metal–heteroelement bond.

All the phosphine derivatives of lanthanides are yellow or orange substances which are stable in an inert atmosphere, but, like the majority of the organolanthanides, hydrolyse extremely readily in moist air.

3. Compounds with Ln–O, Ln–S, and Ln–Se Bonds

The greatest number of publications on derivatives of the Ln–O group referred to β-diketonates and similar chelate complexes. They have been surveyed in a recent review[15] devoted to the Ln–O–C derivatives and will not be considered here. The compounds discussed below include the alkoxides $Ln(OR)_3$, $Cl_xLn(OR)_{3-x}$, and $R'_xLn(OR)_{3-x}$, complexes of the $Ln[M(OR)_4]_3$ series, the mercaptides $Ln(SR)_3$, and thier Se analogues.

The alkoxides $Ln(OR)_3$ are comparatively readily available, are appreciably volatile and soluble, and exhibit a high reactivity, as a result of which they are convenient starting materials for the synthesis of other derivatives. The lanthanide isopropoxides are used particularly frequently. The alkoxides can be obtained by the reaction of the alcohols with the metal, $LnCl_3$, or another alkoxide $Ln(OR')_3$:[181]

$$Ln + 3ROH \rightarrow Ln(OR)_3 + {}^3/_2H_2 ;$$
$$LnCl_3 + 3ROH \xrightarrow{NH_3} Ln(OR)_3 + 3NH_4Cl ;$$
$$Ln(OR')_3 + 3ROH \rightarrow Ln(OR)_3 + 3R'OH .$$

The OR/OR′ exchange is also observed in the reaction of $Ln(OR)_3$ with the esters CH_3COOR' (R′ = alkyl or $SiMe_3$).[182] The reaction of $LnCl_3$ with alkali metal (Li, Na) alkoxides is more convenient for the synthesis of trialkoxides:

$$LnCl_3 + 3MOR \rightarrow Ln(OR)_3 + 3MCl_3 .$$

It is preferable to use NaOR, since LiCl dissolves in the solvents employed more readily than NaCl, which hinders the isolation of the pure $Ln(OR)_3$.

In a recent study[183] it has been shown that scandium, yttrium, and lanthanum tri-isopropoxides can be fairly readily obtained by a direct electrochemical method. The anodic dissolution of the metal is achieved by means of diaphragm-free electrolysis in absolute alcohol with Bu_4NBr as the electrically conducting additive; best results have been obtained using an alternating current.

The alkoxides $Ln(OR)_3$ can exist in the form of monomers and associated coordination species,[183] the degree of association (and hence the volatility and solubility of the alkoxide) being determined by the nature of Ln, the bulk of R, the method of synthesis, and the technique used to isolate the product. With increase of the degree of branching of R, the degree of association diminishes sharply.

The monomeric phenoxides $Ln(OAr)_3$ [Ar = hindered 2,6-di(t-butyl)-4-methylphenyl, Ln = Sc, Y, La, Pr, Nd, Dy, Ho, or Yb] have been synthesised by the usual method, i.e. by the reaction of NaOAr with $LnCl_3$.[184] X-Ray diffraction of the scandium derivative of this series showed that the Sc and O atoms form a planar group; the average O–Sc–O angle is 119.5°.

The use of LiOAr in reactions with lanthanide chlorides with a specific stoichiometry leads to bimetallic complexes with bridging chlorine atoms, namely $[Ln(OAr)_2(\mu\text{-}Cl)_2Li.(THF)_2]$ and $[LnCl(OAr)(\mu\text{-}Cl)_2Li.(THF)_2]$.[122]

The asymmetric cerium(IV) complex $Cp_3CeOPr\text{-}iso$ has been obtained in a low yield by the reaction of cerium tetraisopropoxide with Cp_2Mg.[155]

A characteristic feature of lanthanide alkoxides is their ability to form bimetallic complexes of the type $Ln[M(OR)_4]_3$ (R = iso-Pr; M = Al, Ga, In, or Zr).[15,185] These products are readily soluble and are appreciably volatile (they distil or sublime at 180–200 °C and 0.1 mmHg). They are readily formed on interaction of $LnCl_3$ with $KM(OR)_4$ or with potassium alkoxide in the presence of the salt MCl_3 as well as on simple mixing of the alkoxides $Ln(OR)_3$ and $M(OR)_x$ in alcoholic or tetrahydrofuran solution. The latter reaction was subjected to a detailed investigation,[185] which showed that the complexes can contain solvating alcohol molecules and can have a variable composition with respect to the metals; their solubility changes significantly under these conditions.

The study of the interaction of PhLnI (Ln = Ce, Sm, Eu, or Yb) with the ketones RCOR′ showed[58] that under mild conditions the products are the alkoxides RR′PhCOLnI, which afford the corresponding alcohols after hydrolysis. In the presence of an excess of PhLnI the alkoxide formed is deoxygenated; the hydrolysis product is in this case an olefin. It is noteworthy that in the reaction with a chalcone the PhLnI adds exclusively in the 1,2-positions, while PhLi and PhMgI give rise to both 1,2- and 1,4-adducts.[58]

The first compounds containing an Ln–S bond (thioacetonate, thiocarbamate, and phosphinothioate complexes and thiophenoxides) were obtained at the end of the 1960's.[15,186] The methods of their synthesis do not differ fundamentally from those for the oxygen analogues.

A series of compounds with substituted thiophenyl groups, having the general formula $(iso\text{-}PrO)_{3-x}Ln(SAr)_x$ (Ln = Pr, Nd, or Sm; Ar = 4-ClC_6H_4, 4-t-BuC_6H_4, or 4-t-Bu-2-Me-C_6H_3; x = 1, 2, 3), have been obtained in the reactions of lanthanide tri-isopropoxides with the corresponding phenols for different reactant ratios.[187] The mercaptides derived from the cyclopentadienyl and indenyl complexes Cp_3CeSr and $(C_9H_7)_2Ce(SR)_2$ are known for cerium(IV).[132]

Lanthanide alkylmercaptides were obtained recently[188] via the amido-derivatives:

$$[(Me_3Si)_2N]_3Ln + x\,n\text{-}BuSH \rightarrow [(Me_3Si)_2N]_{3-x}Ln(SBu\text{-}n)_x;$$
$$Ln = Pr, Nd, Sm, Gd;\ x = 1{-}3 .$$

The asymmetric derivatives (x = 1, 2) are readily formed also in the disproportionation reaction between $(R_2N)_3Ln$ and $(n\text{-}BuS)_3Ln$.

The lanthanide organoselenides of the type $(n\text{-}BuSe)_3Ln$ (Ln = Pr, Nd, or Sm) have been synthesised very recently[189] by analogy with the thio-derivatives. Ytterbium(II) butylselenide has been obtained by the reaction of n-BuSeH with $[(Me_3Si)_2N]_2Yb$.

All the symmetrical mercaptides and selenoxides are very sensitive to the action of moisture, are almost insoluble in organic solvents, and, in contrast to the alkoxides, are involatile. On the other hand, the monomercaptides $[(Me_3Si)_2N]_2LnSBu\text{-}n$ sublime *in vacuo* at 140–160 °C and are readily soluble in toluene, THF, and hexane.

In the study of the reactivity of lanthanide compounds relative to small molecules, it was found that the tervalent lanthanide alkoxides, mercaptides, and selenides readily combine with three equivalents of carbon dioxide under normal conditions.[189,190] The addition is accompanied in all cases by the insertion of CO_2 in the Ln–X bond with formation of carbonate, thiocarbonate, and selenocarbonate structures, which is indicated by the appearance of intense absorption bands in the ranges 1530–1580 and 1330–1350 cm^{-1} in the infrared spectra of the products:

$$(t\text{-}BuO)_3Ln + 3CO_2 \rightarrow \quad (t\text{-}BuOCO_2)_3Ln \ ;$$
$$Ln = Pr, Nd, Sm \ .$$

A difference is observed in the reaction of CO_2 with the mercaptides $(n\text{-}BuS)_3Ln$. The addition of the third carbon dioxide molecule is accompanied in this case by the appearance of a band at 2380 cm^{-1} in the infrared spectrum. The high value of this frequency suggests that the third CO_2 molecule adds as a coordinated species. The thiocarbonates readily undergo decarboxylation:[190]

$$(RS)_3Pr \underset{-CO_2;\ 200°}{\overset{+CO_2;\ 20°}{\rightleftarrows}} RSCO_2Pr(SR)_2 \underset{-CO_2;\ 130°}{\overset{+CO_2;\ 20°}{\rightleftarrows}} (RSCO_2)_3PrSR \rightleftarrows$$
$$\underset{-CO_2;\ 90°}{\overset{+CO_2;\ 20°}{\rightleftarrows}} (RSCO_2)_2PrR\cdot CO_2 \ ;$$
$$R = n\text{-}Bu.$$

The decarboxylation of the carbonates $(t\text{-}BuOCO_2)_3Ln$ is accompanied by the side reactions, which render the process irreversible.[190]

4. Compounds with an Ln–M Bond

A report was published in 1971[191] stating that the reaction of metallic erbium with $Hg[Co(CO)_4]_2$ in THF leads to the formation of the product $Er[Co(CO)_4]_3.(THF)_4$. On the basis of infrared spectroscopic data, the authors suggested that the compound contains the Er–Co bond. The same method was used to synthesise the cobalt carbonyl complexes $Ln[Co(CO)_4]_x.(THF)_y$ (Ln = Sm, Eu, Tm, or Yb; $x = 2, 3$; $y = 3, 4$).[192,193] Analogous products containing a variable amount of THF are formed when the free lanthanides react with dinuclear carbonyls[194] or when lanthanide halides react with the anion $Co(CO)_4^-$:[195]

$$Co_2(CO)_8 + Ln \xrightarrow{THF} Ln[Co(CO)_4]_3\cdot(THF)_x;$$
$$M_2(CO)_{10} + Ln \xrightarrow{THF} Ln[M(CO)_5]_3\cdot(THF)_x;$$
$$Ln = Sm, Tm, Yb; \quad M = Mn, Re \ .$$
$$LnCl_3 + 3\,NaCo(CO)_4 \xrightarrow{THF} Ln[Co(CO)_4]_3\cdot(THF)_x;$$
$$Ln = Er, Yb; \ x = 1-4 \ .$$

In the presence of an equimolar reactant ratio, the last reaction gives rise to the formation of the unstable dinuclear compounds $Cl_2LnCo(CO)_4$ (Ln = La, Sm, Dy, Ho, or Yb)[196] and $Cl_2SmM(CO)_5$ (M = Mn or Re).[197]

The easy cleavage of the metal–metal and metal–halogen bonds by metallic lanthanides had also been noted earlier.[198] However, in characterising the lanthanide complexes formed in these reactions, the authors[198] confined themselves to indicating their similarity to Grignard reagents without specifying their structure.

The presence of a direct Ln–M bond has been postulated in all the lanthanide complexes with metal carbonyls indicated above on the basis of the method of their preparation, their reactivity, and their infrared spectra. The exact structure of one of these products, namely $[CpMo(CO)_3]_3La.(THF)_6$, has been recently established by X-ray diffraction.[199] It was found that the La atom is surrounded by three equivalent $CpMo(CO)_3$ fragments and that the bond between the La and Mo atoms is formed via the carbonyl group: Mo–C–O–La. It is natural to suppose that in the erbium analogue $[CpMo(CO)_3]_3Er.(H_2O)_7$ obtained earlier[124] and in the majority of other metal carbonyl complexes of the lanthanides, there is no direct bond between the metal and the lanthanide either. This has been confirmed by structural studies of the cyclopentadienylytterbium complexes $(Me_5C_5)_2YbCo(CO)_4.THF$ and $[(Me_5C_5)_2Yb]_2.[Fe_3(CO)_7(\mu\text{-}CO)_4]$[200,201]), where the presence of a carbonyl bridge has also been established.

One can speak with much confidence about the presence of an Ln–M bond in non-transition metal derivatives. Three main methods for the synthesis of such compounds are known:[2,44,164,202–205]

$$\text{(A)}\ Ln[N(SiMe_3)_2]_3 + 3R_3SnH \xrightarrow{DME} Ln(SnR_3)_3\cdot DME + 3(Me_3Si)_2NH \ ;$$
$$Cl_2LnN(SiMe_3)_2 + R_3SnH \xrightarrow{DME} Cl_2LnSnR_3\cdot DME + (Me_3Si)_2NH \ ;$$
$$Ln = Pr, Nd; \ R = CH_2SiMe_3 \ .$$
$$\text{(B)}\ LnCl_3 + 3LiMPh_3 \rightarrow Ln(MPh_3)_3 + 3LiCl \ ;$$

$$Cp_2LnCl + LiMPh_3 \rightarrow Cp_2LnMPh_3 + LiCl \ ;$$
$$Ln = Pr, Nd, Gd, Er, Yb; \quad M = Ge, Sn \ .$$
$$\text{(C)}\ 7[(C_6F_5)_3M]_2Hg + 2Ln \xrightarrow{DME} 2Ln\{Hg_2[M(C_6F_5)_3]_7\}\cdot(DME)_3 + 3Hg \ ;$$
$$Ln = Pr, Nd, Ho; \ M = Ge, Sn \ .$$

All three methods, (A), (B), and (C), are general and are widely used to synthesise polynuclear compounds, but there are many limitations as regards lanthanide derivatives. Thus, if the germanium hydride Ph_3GeH or triethyltin hydride is used in the Razuvaev–Vyazankin reaction [method (A)], the ether linkage in the solvent (DME) is cleaved and the alkoxides $(R_3M)_xPr(OCH_2CH_2OMe)_{3-x}.DME$ are formed.[202] Compounds obtained by method (B) contain admixtures of side products too difficult to separate (the dicyclopentadienyl complexes, which have been obtained in an analytically pure state, are an exception).[203] The transmetallation reaction [method (C)] requires the presence of electron-accepting substituents at the mercury atom. The complexes obtained by this method are ionic {they comprise the Ln^{3+} cation and anionic species of the type $[(C_6F_5)_3Ge]_3Hg^-$ and $[(C_6F_5)_3Ge]_4Hg^{2-}$} and do not contain, as suggested initially,[204] a direct Ln–Ge bond. Praseodymium does not interact (at 100°, 10 h) with compounds which do not contain electron-accepting substituents, namely $(Et_3Ge)_2Hg$, $(Ph_3Ge)_2Hg$, and $[(Me_3SiCH_2)_3Sn]_2Hg$.[205]

Analogous ionic complexes have been obtained by method (A).[206,207] This is the first example of the synthesis of ionic compounds by the hydride method. The reaction between the lanthanide alkoxide and the hydrogermane is carried out in the presence of acceptors of the germyl anions $(C_6F_4)_3Ge^-$ formed in the first stage of the process. Trinuclear compounds with pentafluorophenyl substituents are used as such acceptors:

$$3(C_6F_5)_3GeH + \quad (t\text{-}BuO)_3Pr + 2[(C_6F_5)_3M]_2M' \xrightarrow{DME}$$
$$\rightarrow\{[(C_6F_5)_3Ge]_3[(C_6F_5)_3M]_4M'_2\}Pr\cdot(DME)_3 + 3\ t\text{-}BuOH;$$
$$M = Si, Ge, Sn; \quad M' = Cd, Hg \ .$$

$(C_6F_5)_3SnH$ reacts analogously. The bifunctional hydrides $(C_6F_5)_2GeH_2$ and $(C_6F_5)_2Ge(H)Ge(C_6F_5)_2H$ produces, in such processes, more involved complexes with anions incorporating up to 10 germanium and mercury atoms.[208]

The disproportionation reaction, which is characteristic of lanthanide derivatives, makes it possible to convert the trisubstituted complexes into asymmetric products:[164]

$$2[(Me_3Si)_2N]_3Pr + [(Me_3SiCH_2)_3Sn]_3Pr\cdot DME \xrightarrow{DME}$$
$$\rightarrow 3[(Me_3Si)_2N]_3PrSn(CH_2SiMe_3)_3\cdot{}^1/_2\ DME \ .$$

All the compounds with the Ln–M group are solids, which are unstable in air and are sparingly soluble in aliphatic and aromatic hydrocarbons; they melt with decomposition on heating to temperatures above 150–200 °C. Their reactivity

has been investigated mainly in relation to $[(Me_3SiCH_2)_3Sn]_3Pr.DME$[202] and $\{[(C_6F_5)_3Ge]_7Hg_2\}Pr.(DME)_3$:[205]

$$(R_3Sn)_3Pr\cdot DME \begin{cases} \xrightarrow[50^\circ]{H_2O} R_3SnMe + (R_3Sn)_2O + Pr(OH)_3 ; \\ \xrightarrow[20^\circ]{HCl} R_3SnMe + R_3SnCl + PrCl_3 + H_2 ; \\ \xrightarrow[120^\circ]{BrCH_2CH_2Br} R_3SnSnR_3 + PrBr_3 + H_2C{=}CH_2 ; \\ \xrightarrow[50^\circ]{(PhCOO)_2} R_3SnOCOPh + R_3SnPr(OCOPh)_2 ; \\ \xrightarrow{CF_3COOAg} R_3SnOCOCF_3 + (CF_3COO)_3Pr + Ag . \end{cases}$$

When the hydrolysis is carried out under milder conditions (20 °C, 30 min), one Sn–Pr bond is retained. The complex $R_3SnPr(OH)_2$ formed is stable in air like the benzoyloxy-derivative $R_3SnPr(OCOPh)_2$, in contrast to the majority of organometallic lanthanide derivatives.

It has been found recently[169] that stannyl-lanthanide complexes combine with carbon dioxide at 20 °C under normal pressure:

$$(R_3Sn)_xPr[N(SiMe_3)_2]_{3-x}\cdot DME + 2CO_2 \rightarrow (R_3Sn)_xPr[N(SiMe_3)_2]_{3-x}\cdot 2CO_2\cdot DME$$
$$x = 1, 3;\ R = CH_2SiMe_3 .$$

The infrared spectra of the adducts contain absorption bands characteristic of coordinated CO_2 (at 2180, 1620, and 1520 cm^{-1}). It is of interest to note that, depending on the conditions, the hydrolysis of these complexes may be accompanied by carbon dioxide evolution or can give rise to a new CO_2-containing product: $R_3SnPr(OH)_2.2CO_2$.

Lanthanide germylmercurates do not combine with carbon dioxide under comparable conditions. Their reactions with hydrogen chloride have been used to determined their structures:[205]

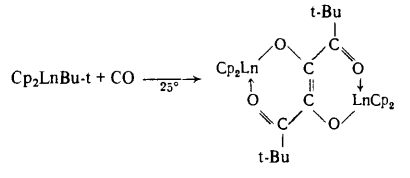
$$\left\{\begin{matrix}[(C_6F_5)_3Ge]_8Hg^- \\ [(C_6F_5)_3Ge]_4Hg^{2-}\end{matrix}\right\} Pr^{3+}\cdot(DME)_3 \begin{cases} \xrightarrow{1HCl} (C_6F_5)_3GeH + \{[(C_6F_5)_3Ge]_4Hg\}PrCl\times \\ \times(DME)_3 + [(C_6F_5)_3Ge]_2Hg \\ \xrightarrow{3HCl} 3(C_6F_5)_3GeH + PrCl_3 + \\ + 2[(C_6F_5)_3Ge]_2Hg ; \\ \xrightarrow{(excess)\ HCl} 5(C_6F_5)_3GeH + 2(C_6F_5)_3GeCl + \\ + 2Hg + PrCl_3 . \end{cases}$$

It is seen from the equations presented above that the ionic groups are the first to decompose.

VI. OTHER COMPOUNDS

The cocodensation of lanthanide vapour with CO in an argon matrix at 4 K leads to the formation of extremely unstable metal carbonyls of the type $Ln(CO)_x$ ($x = 1–6$).[209,210] Analysis of the infrared spectra of these complexes showed that they resemble transition metal carbonyls.

An interesting dionediolate complex has been obtained by the reaction of $Cp_2LnBu\text{-}t$ with an excess of carbon monoxide.[211] The structure of the product has been postulated on the basis of X-ray diffraction data:



Use of 1-pyrazolyl borate ligands frequently makes it possible to obtain unusually high coordination numbers of the metal atoms, for example, six in the case of tin.[212] The interaction of $KHB(C_3H_3N_2)_2$ with $LnCl_3(H_2O)_x$ in water leads to crystalline anhydrous complexes $Ln[HB(C_3H_3N_2)_3]_3$ (Ln = Y, La, Ce, Pr, Sm, Gd, or Er).[213] The asymmetric complexes $Cl_2Er[HB(C_3H_3N_2)_3]$ and $ClEr[HB(C_3H_3N_2)_3]_2$ have been synthesised from anhydrous erbium chloride in THF.

Until recently, only halide clusters of the type Er_7I_{10} were known in the series of lanthanides.[214] However, the first carbon-containing lanthanide clusters, namely $Gd_{10}C_4Cl_{18}$ and $Gd_{10}C_4Cl_{17}$, were obtained in 1982 and their structures were characterised.[215] They are formed in an overall yield of 90% on heating stoichiometric amounts of $GdCl_3$, Gd, and graphite to 800–850 °C. The metallic skeleton of these clusters is made up to two Gd_6 octahedra having a common edge. All the accessible faces of the octahedra are centred on binary carbon groups C_2 with a C–C distance of 1.47 Å and have bridging chlorine atoms. The Gd–Gd bond length is in the range 3.212–4.086 Å for $Gd_{10}C_4Cl_{18}$ and 3.121–4.014 Å for $Gd_{10}C_4Cl_{17}$ (the atomic radius of gadolinium is 1.79 Å).

VII. APPLICATIONS OF ORGANOLANTHANIDES

The principal field in which organic derivatives of the lanthanides are used is catalytic reactions. The catalytic properties of inorganic lanthanide compounds have been known for a long time and have been used in a wide variety of processes, such as the cracking of petroleum, the hydrogenation and dehydrogenation of hydrocarbons, the isomerisation of olefins, the dehydration of alcohols, the synthesis of ketones from alcohols and acids, the cracking of alkanes, the emulsion of polymerisation of acrylonitrile, the manufacture of nylon, etc.[8] The olefin and diolefin polymerisation processes in which catalysts based on the lanthanides as a rule exhibit a higher activity and stereospecificity than other catalytic systems, are the most important.

In the middle 1960's it was observed that a mixture of $LnCl_3$ (Ln = Y, La, Ce, Pr, Nd, Sm, Gd, Er, or Yb) and trialkylaluminium induces the polymerisation of butadiene under mild conditions with the preferenital (>95%) formation of 1,4-*cis*-polybutadiene.[216] Studies on these lines have developed greatly and have now reached the level of industrial application. It has been established that, apart from the mixture inidcated above, stereospecific polymerisation and copolymerisation of diolefins are catalysed by the $LnCl_3.xL/R_3Al$[217–219] and cerium octanoate/R_3Al/halogen[220] systems and by lanthanide phosphates, naphthenates, and carboxylates mixed with R_3Al and a halogen.[219]

Systems based on the "light" lanthanides (Ce, Pr, and Nd) show the highest activity. Catalysts with bivalent lanthanides are inactive. The addition of a small amount of alcohol to the $LnCl_3/R_3Al$ binary system appreciably increases its activity without altering its stereospecificity.[221] It has been found that a new effective catalyst, namely $LnCl_3.3ROH/R_3Al$, is formed under these conditions. Allyl complexes of the type $LiLn(C_3H_7)_4.$dioxan (Ln = Ce, Nd, Sn, Gd, or Dy) induce the rapid and far-reaching polymerisation of butadiene.[8] A stereoregular 1,4-polymer is also formed in this instance, but (in contrast to the catalyst quoted above) it has the *trans*-structure to the extent of 80–90%. The 1,4-*trans*-polymer is also obtained in the presence of tribenzylneodymium etherate $(PhCH_2)_3Nd.(Et_2O)_3$.[40] It has been suggested that all three Nd–C bonds participate in the polymerisation with formation of tricrotyl- (or tri-isopropenyl)-neodymium complexes in the intermediate stages.

The LnX_3/R_3Al, $LnX_3(LnO)/RLi(RMgX)$, $Ln/Mo_2O_3/Al_2O_3$, $Ln(acac)_3/R_3\text{-}_mAlX_mPPh_3$, LnO/MH,[8] $(Me_5C_5)_2Ln.L$, and $(Me_5C_5)_2LnMe$ (Ln = Sm, Eu, Yb, or Lu; L = Et_2O, THF, or R_3Al) systems are used for the polymerisation of ethylene and its derivatives.[222] Weak catalytic properties have been

observed also in catalysts of the Ziegler–Natta type containing the cyclo-octatetraenylcerium complexes $Ce(C_8H_8)_2$, $Ce_2(C_8H_8)_3$, and $C_8H_8Ce(O\text{-}Pr\text{-}iso)_2AlEt_2$. The dimeric complexes $[(RC_5H_4)_2LnMe]_2$ and $(RC_5H_4)_2LnMe_2AlMe_2$ (Ln = Y, Ho, Er, or Yb; R = H, Me, or $SiMe_3$) are effective homogeneous catalysts of the polymerisation of ethylene.[87] The processes take place at 75 °C and 5 atm in the presence of the lanthanide complex and at 95° and 33 atm in the presence of an aluminium-containing catalyst.

The stereospecific polymerisation of phenylacetylene with formation of the *cis*-polymer (80–100%) in the presence of systems comprising lanthanide naphthenate or phosphonate complexes and R_3Al, sometimes with the addition of a third component, has been mentioned.[223]

Thus, in all the catalytic lanthanide systems active in the polymerisation reactions of unsaturated hydrocarbons, an Ln–C bond is present or is formed in the initial stages of the process. A study of the mechanism of these processes in relation to the model reaction of $(Me_5C_5)_2LuMe.Et_2O$ with propene[78] and of the thermal decomposition of the butyl derivative $(Me_5C_5)_2LuBu$ [224] enabled the authors of these investigations to propose a general mechanism of polymerisation in the presence of organolanthanide catalysts. Three main reaction pathways involving the Ln–R groups have been suggested: (a) the insertion of the olefin with formation of Ln–C–C–R; (b) the β-hydride decomposition of Ln–R and the subsequent insertion of the olefin in the Ln–H bond with formation of Ln–C–C–H; (c) the β-alkyl decomposition of Ln–R and the subsequent insertion of the olefin in the Ln–R′ bond. One should note that, in the presence of coordinated ligands in the catalyst molecule, the above stages are preceded by the dissociation of the Ln ← L bond.[78,222] This mechanism of the polymerisation of olefins in the presence of organic derivatives of the lanthanides is consistent with other data, for example, the incorporation of CO_2 in the oligomeric complex $Ln–(CH_2)_x–Me$, which leads to the corresponding acids $Me–(CH_2)_x–COOH$ after hydrolysis.[219]

The complexes formed on cocodensation of the vapours of the lanthanide (Nd, Sm, Er, and Yb) and acetylene derivatives RC ≡ CR′ catalyse the hydrogenation of alkenes and alkynes by hydrogen under normal conditions.[26,95,108,225] The mechanism of these reactions, proposed by Evans et al,[26] involves the formation of the lanthanide hydride in the initial stage:

$$Ln–R + H_2 \rightarrow Ln–H + RH \quad ;$$

$$Ln–H + RC{\equiv}CR \rightarrow \underset{R}{\overset{Ln}{}}\!\!>C{=}C<\!\!\underset{R}{\overset{H}{}} \quad ;$$

$$\underset{R}{\overset{Ln}{}}\!\!>C{=}C<\!\!\underset{R}{\overset{H}{}} + H_2 \rightarrow \underset{R}{\overset{H}{}}\!\!>C{=}C<\!\!\underset{R}{\overset{H}{}} \quad .$$

The complexes formed when the SmMg alloy is treated with anthracene in THF[226] and the alloy $LaNi_5$ [227] are also capable of activating molecular hydrogen. Both compounds readily absorb hydrogen to form hydrides and the latter reduce olefins to alkanes under mild conditions.

The lanthanide salts have marked catalytic properties. For example, SmI_2 and YbI_2 catalyse the deoxygenation of epoxides and sulphoxides, the reduction of aldehydes, the conversion of alkyl halides into alkanes, and the synthesis of tertiary alcohols from ketones and RX.[228,229] The salts of tervalent lanthanides promote or catalyse the oxidation of benzoins to benzils,[230] the formation of pyrimidine,[231] and the selective 1,2-reduction of conjugated ketones by sodium tetrahydroborate.[232] It has been found that lanthanum, cerium, praseodymium, neodymium, and samarium β-nitroso-α-naphthoxides, deposited on alumina, catalyse the dehydrohalogenation of 3,4-dichlorobut-1-ene to give chloroprene.[233]

In the above processes the initial catalysts are inorganic derivatives, but organolanthanides are apparently formed in all cases as intermediates.

Cerium amalgam readily reacts with alkyl and benzyl iodides in a ketone to form the tertiary alcohol $H_2C = CHCH_2C(R).(R')OH$ or $PhCH_2C(R)(R')OH$.[234] These reactions demonstrate the preparative possibilities of the lanthanides.

The use of organic derivatives of lanthanides as antiknocking agents in motor fuels is promising.[8] Particularly satisfactory results have been obtained for cerium, praseodymium, neodymium, and ytterbium, 2,2,6,6-tetramethylhepta-3,5-dionates whose antiknocking properties are superior to those of tetraethyl-lead.

The β-diketonates and similar chelate complexes of the lanthanides have also found extensive applications as shift reagents in NMR spectroscopy.[235]

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Russian Chemical Reviews

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This issue is devoted to the 70th anniversary of the birth of the outstanding Soviet scientist Academician Nikolai Markovich Emanuel' who directed the journal "Uspekhi Khimii" from 1972 until the last days of his life.

Emanuel"s scientific interests embraced many fields of science: the chemical physics of the liquid-phase oxidation of organic substances; elementary reactions and kinetics of processes in the condensed phase; the ageing and stabilisation of polymers; the kinetics of biological, mainly pathological, processes.

The issue includes articles by a number of the pupils of Academicain Emanuel'. They demonstrate the breadth of his thought and a surprising ability to foresee the scientific prospects for the development of particular branches of science.

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The Chemical Physics of the Ageing and Stabilisation of Elastomers

N.M.Emanuel' (deceased)

The ageing and stabilisation of elastomers are considered from the standpoint of chemical physics. A general method for the fitting to the kinetic curves of relations characterising the ageing of elastomers under the influence of oxygen, light, ozone, and mechanical stresses is discussed. Different principles and procedures for the stabilisation of elastomers are analysed. The bibliography includes 75 references.

CONTENTS

I.	Introduction	817
II.	A general method for the fitting of equations to kinetic curves	818
III.	Thermo-oxidative ageing of elastomers	820
IV.	Photo-oxidative ageing of elastomers	825
V.	Ozone-induced ageing of elastomers	830
VI.	The influence of mechanical stresses on the kinetics of the reactions of elastomers	832
VII.	The role of radical reactions in the wear of vulcanised elastomers	833

INTRODUCTION

Modern chemistry is concerned primarily with new materials for various branches of technology, agriculture, and ordinary life. Elastomers occupy one of the leading positions among such materials and the range of articles based on them is extremely wide.[1] The world production of different types of rubber in 1984 amounted to 14 million tonnes.[2]

The principal deficiency of the majority of elastomers is rapid ageing under operating conditions. Thus, when anticorrosion measures are taken, metals last for 15 and more years. Elastomers and articles prepared from them have in most cases a much shorter useful life.

Ageing is known to be a process which develops with time, i.e. the study of its mechanism is the subject to chemical kinetics. The knowledge of the mechanism of ageing makes it possible to solve rationally the problem of increasing the life of the articles and to predict their likely usefulness under various conditions.

Research into the kinetics and mechanism of the ageing and stabilisation of polymeric materials has developed in recent years on a broad front. A new field in the chemistry of macromolecular compounds, namely the chemical physics of the ageing and stabilisation of polymers, was initiated on the basis of these investigations.[3-5] It includes the study not only of the elementary reactions and macroscopic stages

in the ageing and stabilisation but also the role in these processes of the physical organisation of the polymer, the dynamics of molecular movements, and other physical factors which determine the operating properties of polymeric materials.

In the course of the processing, storage, and use elastomers are acted upon by numerous external factors which cause the initiation and development of chemical and physical processes leading to the alteration of the operating properties (Fig.1). At the present time it is possible to indicate which particular ageing factors act on particular articles containing elastomers (Fig.2). The principal elementary stages in the ageing process, the types of stabilisers, and the mode of their action are also known (Fig.3).

The aim of the present review is to describe the state of the principal trends in the chemical physics of the ageing and stabilisation of elastomers.

II. A GENERAL METHOD FOR THE FITTING OF EQUATIONS TO KINETIC CURVES

In the study of the ageing of elastomers under both natural and artificial conditions, various kinetic relations describing the variation of the parameters of the operating properties of materials or parameters indirectly related to these properties (for example, the absorption of oxygen in

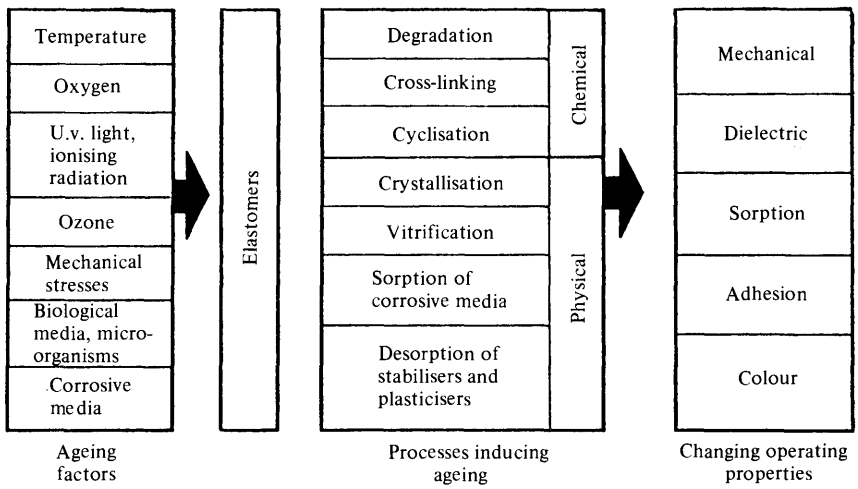


Figure 1. The effect of external factors and the changes in the operating properties of articles as a result of the ageing of elastomers.

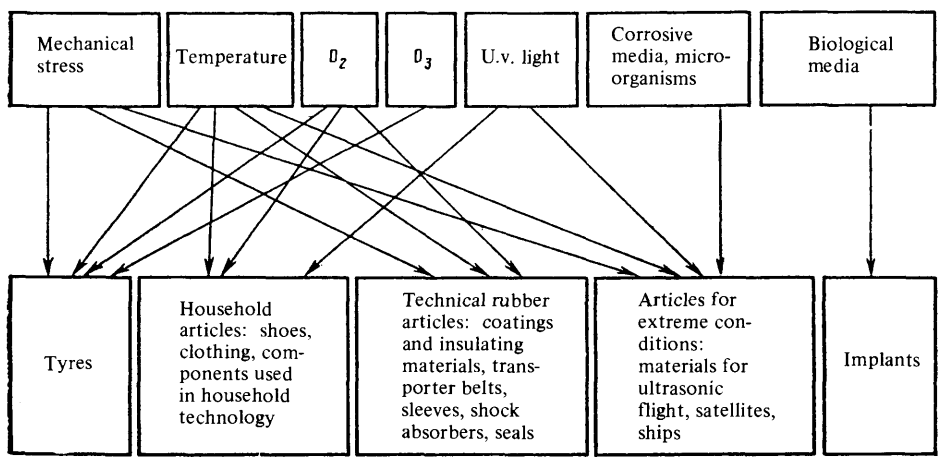


Figure 2. Principal types of articles based on elastomers and the external factors inducing their ageing.

thermo-oxidative ageing, the decrease of the mass of the specimen in thermal degradation, etc.) are obtained.

Extensive experimental data on the kinetics of the ageing of polymers, including elastomers, have now been accumulated. Various types of kinetic curves are known. As an illustration, Fig.4 presents several experimental curves for the ageing of various elastomers.[6-11] In a formal kinetic description of the ageing of polymers, it is of interest to obtain generalised kinetic curves which would make it possible, on the one hand, to classify a set of experimental data, and, on the other hand, would permit the solution of many problems of practical importance, for example the prediction of the behaviour of the operating properties during ageing.

Mathematical functions describing satisfactorily each of the above types of kinetic curves are known. A particular function can be chosen either on the basis of the known process mechanism or on the basis of analogies or an empirical selection by fitting equations to experimental data using the familiar methods of regression analysis.

A wide variety of chemical and physical processes take place in the polymeric material during ageing but under the real storage and operating conditions only some of them alter the operating properties. In many cases the changes in the operating properties can therefore be attributed to the occurrence of specific processes.

The decrease of the tensile strength σ in the high-temperature ageing of polymeric materials is mainly caused by degradation reactions and is described satisfactorily by the equation

$$\varphi = \exp(-\alpha t), \qquad (1)$$

where $\phi = (\sigma/\sigma_\infty - 1)(\sigma_0/\sigma_\infty - 1)^{-1}$, α is the transformation coefficient, and σ_0 and σ_∞ are the initial and limiting

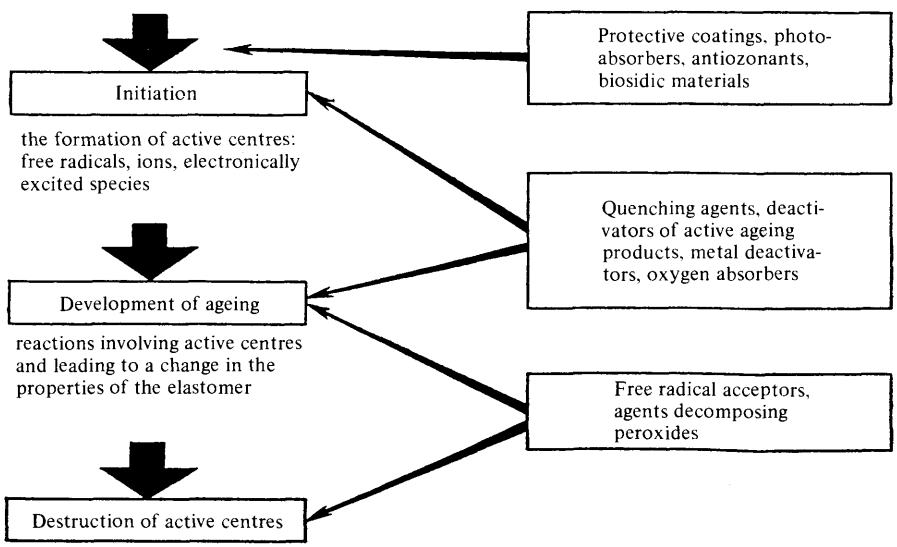


Figure 3. Principal elementary stages in the ageing of elastomers, the types of stabilisers, and the mode of their action.

stresses. Fig.5 presents a generalised kinetic curve for the decrease of ϕ in the ageing of various plastics and elastomers.[12] The deformation caused both by cross-linking and degradation reactions increases during the ageing of elastomers. The accumulation of the residual deformation ε is described by the equation

$$\psi = 1 - \exp(-\alpha t), \qquad (2)$$

where $\psi = (\varepsilon/\varepsilon_0 - 1)(\varepsilon_\infty/\varepsilon_0 - 1)^{-1}$. The generalised kinetic curve for a series of elastomers is illustrated in Fig.6.

III. THERMO-OXIDATIVE AGEING OF ELASTOMERS

A large set of data for the thermo-oxidative ageing of elastomers, some of which have been surveyed in monographs and reviews,[13-21] has now accumulated. The kinetics of the absorption of oxygen are most frequently studied in thermo-oxidative ageing.

1. Formal Kinetics of Thermo-oxidative Ageing

Analysis of the experimental data for the absorption of oxygen in the thermo-oxidative ageing of various polymers in both open and closed systems has shown that three main types of kinetic curves are encountered: curves of the autoaccelerating type, curves which decrease exponentially with time, and S-shaped kinetic curves.[22]

Kinetic curves of the first type are characteristic of the absorption of oxygen in the thermal oxidation of elastomers at temperatures below 200 °C; they are described by the equation

$$N_{O_2} = a(t - \tau)^2, \qquad (3)$$

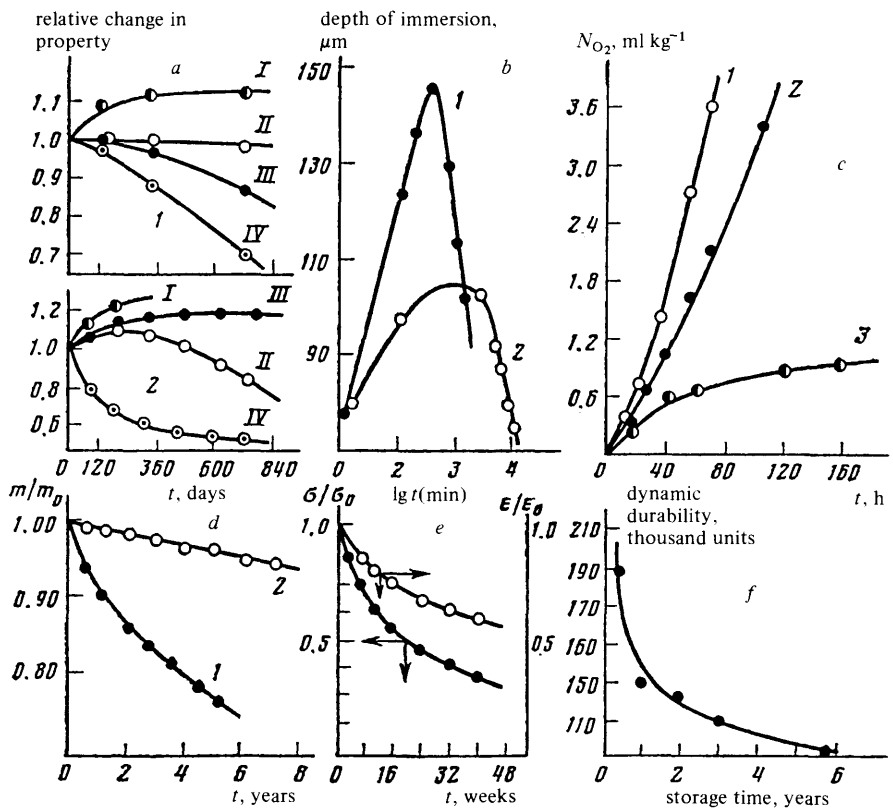


Figure 4. Kinetic relations obtained in the ageing of various elastomers: *a*) changes in the mechanical properties of raw rubber specimens during natural ageing in a climatic station: 1) butyl rubber; 2) butadiene-acrylonitrile rubber [I) Young's modulus; II) tensile strength; III) microhardness; IV) deformation on rupture]; *b*) changes in the microhardness of rubbers based on the raw butadiene-nitrile rubber in transformer oil during wear by rubbing: 1) 170 °C; 2) 120 °C; *c*) absorption of oxygen by the natural rubber latex containing 2% of 3,5-di-t-butyl-4-hydroxybenzyl acrylate at 70 °C: 1) without antioxidant; 2) antioxidant introduced mechanically; 3) antioxidant bound chemically to the raw rubber macromolecules; *d*) changes in the mass of polydimethylsiloxane (curve *1*) and segmented polyurethane (curve *2*) after implantation into a subcutaneous cell in rabbit; *e*) changes in the mechanical properties of specimens of a fluoro-silicone elastomer (Dow Corning, USA) at 200 °C; *f*) changes in the dynamic durability of protective rubber based on butadiene–styrene raw rubber during storage in an unheated space.

where N_{O_2} is the amount of oxygen absorbed by the polymer, a is a constant, and τ is the induction period. The parameters a and τ depend on the structure of the polymer, the oxygen pressure, and temperature. The equation is valid for low degrees of oxidation.

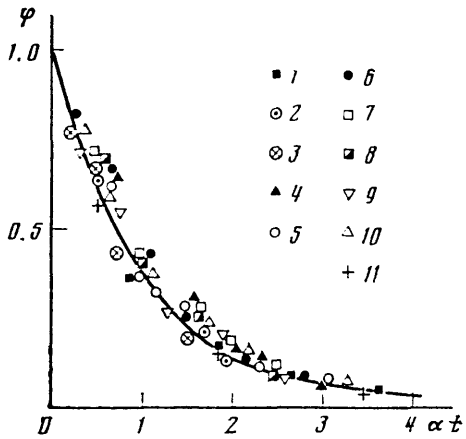
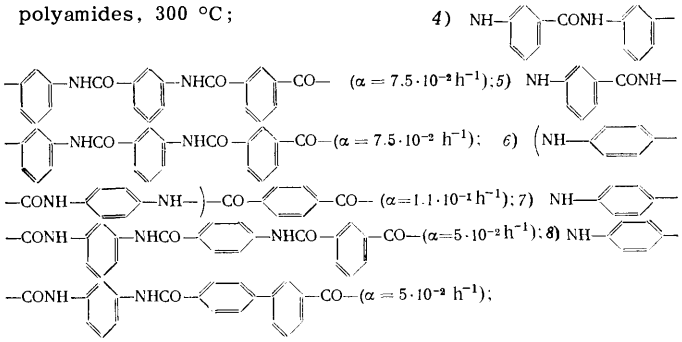


Figure 5. Generalised kinetic curve for the decrease of the tensile strength during the ageing of various plastics and elastomers: *1*) polyimide composite, 300 °C ($\alpha = 3.8 \times 10^{-3}$ h^{-1}); *2*) phenylon, 220–250 °C ($\alpha = 1.6 \times 10^{-3}$ h^{-1}); *3*) capton-H film, 300 °C ($\alpha = 2.6 \times 10^{-1}$ $week^{-1}$); aromatic polyamides, 300 °C;



rubbers based on different raw rubbers; *9*) butadiene–sytrene, 90 °C ($\alpha = 3.5 \times 10^{-3}$ h^{-1}); *10*) butadiene–nitrile, 20 °C ($\alpha = 0.1$ $year^{-1}$); *11*) isoprene, 100 °C ($\alpha = 2.8 \times 10^{-2}$ h^{-1}).

Fig.7 presents the generalised kinetic curve for the absorption of O_2 in the oxidation of various polymers, including elastomers, at 90–200 °C. Kinetic curves of an analogous type can be obtained for the thermal oxidation of vulcanised elastomers with different contents of technical carbon[23] and vulcanised elastomers with different structures of the main chain in the network,[24] and also kinetic curves recorded at different partial pressures of oxygen[25] and for vulcanised elastomers with different amounts of bound sulphur.[26]

An equation relating the change in the mechanical properties (tensile strength and elongation on rupture) to the absorption of oxygen and the accumulation of oxygen-containing groups in the polymer has been obtained for polyolefins.[27] Fig.8 presents analogous experimental data obtained in the thermal oxidation of vulcanised butadiene–styrene rubber.[21]

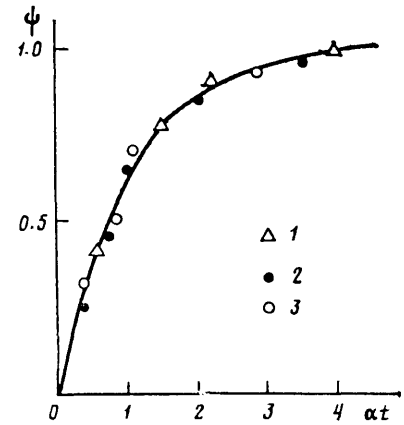


Figure 6. Generalised kinetic curve for the increase of the residual deformation during the ageing of various rubbers based on different polymers: *1*) butadiene–styrene, vacuum, 90 °C ($\alpha = 0.1$ day^{-1}); *2*) butadiene–styrene, 120 atm, 70 °C ($\alpha = 0.2$ day^{-1}); *3*) butadiene–acrylonitrile, SKI-18, ammonia, 20 °C ($\alpha = 3.5 \times 10^{-2}$ day^{-1}).

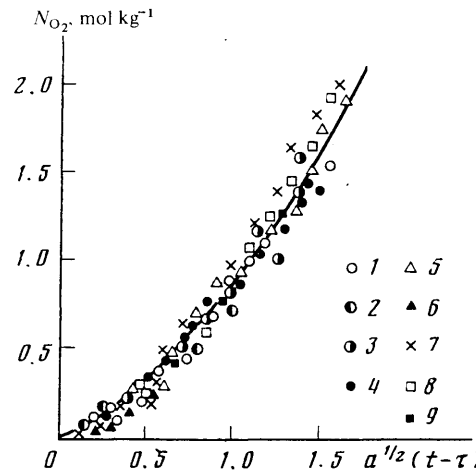


Figure 7. Generalised kinetic curve for the absorption of oxygen in the oxidation of various polymers: *1*) polyethylene (90 °C); *2*) polypropylene (130 °C); *3*) ethylene–propene copolymer (130 °C); *4*) poly-4-methylpent-1-ene (130 °C); *5*) vulcanised natural rubber (110 °C); *6*) polystyrene (160°); *7*) polyheptene (100 °C); *8*) polynon-1-ene (100 °C).

It has been suggested that the thermo-oxidative stability of polymers be characterised by the temperature at which 0.1 mol kg^{-1} of oxygen is absorbed in air in the course of 15 min[27] (Table 1). The values of 0.1 mol kg^{-1} was selected

because in the presence of this amount of absorbed oxygen the chemical and physical properties of polymers begin to change appreciably.

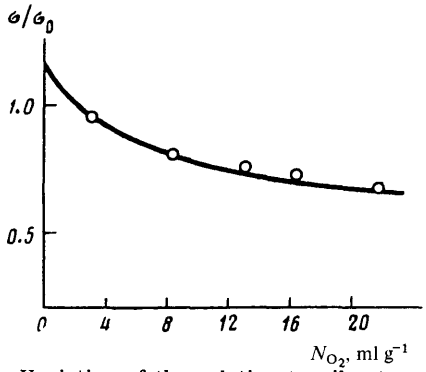


Figure 8. Variation of the relative tensile strength of vulcanised butadiene–styrene rubber as a function of the amount of oxygen absorbed at 110 °C and an oxygen pressure of 1 atm.

Table 1. The thermo-oxidative stability of carbochain polymers.

Polymer	$T_{1/2}$*, °C	Polymer	$T_{1/2}$*, °C
Polypropylene	135	Poly-4-methylpent-1-ene	165
Polyisoprene	135	Polyethylene	170
Polybutadiene	155	Polystyrene	205
Poly(methyl methacrylate)	160	Poly(vinyl chloride)	210

*The temperature corresponding to the absorption of 0.1 mol kg^{-1} of oxygen in 15 min.

2. Characteristic Features of the Solid-Phase Reactions in the Thermo-oxidative Ageing of Elastomers

Kinetic studies of the thermo-oxidative ageing of elastomers have always been based on the theoretical ideas concerning the liquid-phase oxidation reactions of hydrocarbons. Numerous investigations established that the liquid-phase oxidation of hydrocarbons is a degenerate-branched chain process.[4,28–30] However, the thermal oxidation of elastomers, like that of other polymers, shows many differences from the liquid-phase oxidation of hydrocarbons despite the similarity of the kinetics and the reaction products. Elastomers may contain domain structures—structurally similar groups segregated to form a microheterophase, while in filled elastomers there is a phase consisting of "hard" rubber adsorbed on the filler.[31,32] Such inhomogeneity of the physical structures of elastomers and the occurrence of solid-phase reactions give rise to the following characteristic features of the thermo-oxidative ageing of solid elastomers.

1. The inhomogeneity of the three-dimensional distribution of the active centres and reactants (oxygen, radicals, and stabilisers).

2. The structural-kinetic inhomogeneity, i.e. the distribution of regions differing in the frequencies and amplitudes of molecular movements, which influence the kinetics of radical processes.

3. Slow migration of segments of the macromolecules in polymers diminishes the rate of emergence of the radicals from the cage compared with a liquid and the probability of the radical recombination within the cage is greater in elastomers than in a liquid, i.e. the cage effect is more marked.

4. The slower diffusion of oxygen in polymers compared with liquid hydrocarbons is responsible for the specific features of the reactions of alkyl macroradicals which not only react with oxygen, as happens in hydrocarbons undergoing oxidation, but also enter into a whole series of other reactions: they isomerise, abstract hydrogen atoms from neighbouring C–H bonds, and react with hydroperoxides.[33]

5. In a liquid the R and RO_2 radicals migrate by diffusing; in solid polymers the diffusion of free-radical species is slow and other mechanisms of the migration of a free valence may operate—the relay migration and the transfer of the free valence by low-molecular-weight radicals and molecules.[1,34,35] The relative contributions of these mechanisms depend on the oxidation conditions and the structure of the elastomer.

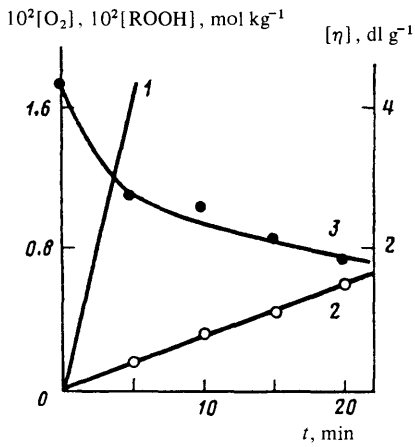
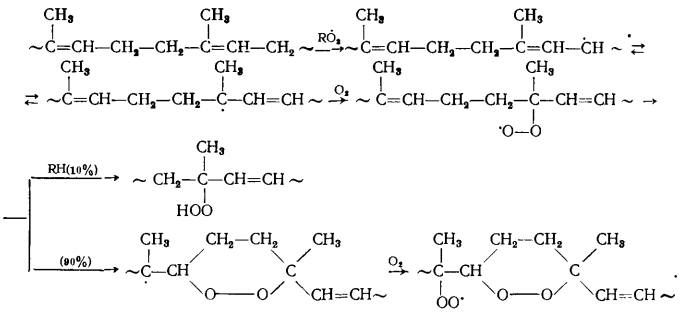


Figure 9. Kinetics of the absorption of oxygen (curve *1*), the accumulation of hydroperoxides (curve *2*), and the changes in the intrinsic viscosity of *cis*-1,4-polyisoprene (curve *3*) at 80 °C, $[DAC]_0 = 0.06$ M.

3. The Mechanism of the Thermo-oxidative Degradation of Polydienes

In the thermo-oxidative degradation of *cis*-1,4-polyisoprene only part of the absorbed oxygen is consumed in the formation of hydroperoxy-groups (Fig.9). This is associated with the propagation of the oxidation chain in two directions:[36,37] (a) via a reaction involving the intramolecular addition of the peroxy-radical to the double bond with formation of a cyclic peroxide with a rate constant k_p; (b) via the reaction involving the abstraction of a hydrogen atom from the α-methylene group with formation of a hydroperoxide (k_p'). The overall scheme includes the following

reactions:



The ratio $k'_p/k_p[RH] = 8.3$ for *cis*-1,4-polyisoprene.[37]

Oxidation results in the formation of peroxy-macroradicals in which peroxide bridges adjoin the free valence. Such structural fragments, which have been identified by NMR, are unstable and constitute centres for the degradation of polyisoprene via the scheme

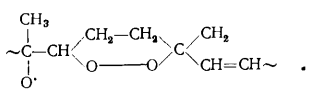
$$2R\dot{O}_2 \rightarrow 2R\dot{O},$$
$$R\dot{O} \rightarrow \text{degradation}.$$

According to this scheme, the rate of degradation is proportional to the rate of initiation;[37] the proportionality coefficient, measured in experiments on the initiated degradation of polyisoprene, is 15, i.e. the decomposition of the RO macroradicals formed is 15 times faster than the chain termination in the polyisoprene being oxidised.[37]

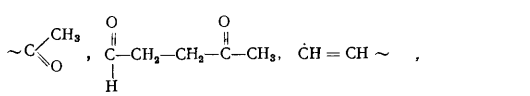
The kinetics of the oxidative degradation of polyisoprene in the presence of inhibitors have been investigated.[38] It was found that, in the presence of an inhibitor (phenol or aromatic amine), a new source of degradation appears, namely the reaction of the peroxy-macroradical with the inhibitor radical Iṅ:

$$R\dot{O}_2 + I\dot{n} \rightarrow ROOIn \rightarrow R\dot{O} + In\dot{O};$$
$$R\dot{O} \rightarrow \text{degradation}.$$

The radical ṘO has the structure



Its decomposition results in the formation of the groups



Together with the mechanism of the oxidative degradation described above, there is a possibility of another mechanism, according to which the polyisoprene degradation centres are the allyloxy-radicals formed on decomposition of the hydroperoxy-groups.[39]

4. Stabilisation of Elastomers

The stabilisation of elastomers has attracted continuous attention for many years and numerous studies have been devoted to the mechanism of the action of stabilisers. Two main types of antioxidants, which cause chain termination, are known: electron donors and proton donors. It has been shown by infrared spectroscopy that phenols and aromatic amines with bulky substituents are present in the matrices of polydiene elastomers as weak π-complexes with the double bonds.[40]

The mechanism of action of the antioxidant in the oxidation of elastomers depends on its concentration in the polymer. In the concentration range from 4.5×10^{-4} to 4.5×10^{-3} mol kg^{-1} the oxidation of *cis*-1,4-polyisoprene in the presence of sterically hindered phenols proceeds as a chain reaction with chain termination by the inhibitor molecules; the effectiveness of antioxidants in the polymer is close to that in hydrocarbon media (Table 2).[38]

Table 2. Kinetic parameters of the chain termination by phenolic antioxidants in the inhibited oxidation reactions of *cis*-1,4-polyisoprene (80 °C, $p_{O_2} = 10^5$ Pa).

Antioxidant	f	$k_2k_6^{-1/2}$, kg$^{1/2}$ mol$^{-1/2}$ s$^{1/2}$
2,6-Di-t-butyl-4-methylphenol	2.0	42.6±10.4
2,2-Methylenebis(6-t-butyl-4-methylphenol)	2.6	42.1±9.9
4,4-Methylenebis(2,6-di-t-butylphenol)	2.7	37.9±12.9
2,4,6-Tris(3,5-di-t-butyl-4-hydroxyphenyl)-1,3,5-trimethylbenzene	1.9	28.9±6.4
Ester of 3,5-di-t-butyl-4-hydroxyphenylpropionic acid and pentaerythritol	2.0	38.8±4 5

The rate of the inhibited chain oxidation is

$$W_{O_2} = \frac{k_2[RH]W_0}{fk_7[InH]_0}, \quad (4)$$

where W_0 is the rate of initiation and f the inhibition coefficient, i.e. the number of kinetic chains terminated by one antioxidant molecule.

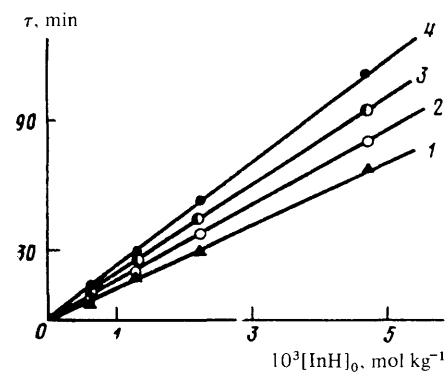


Figure 10. Dependence of the induction period in the oxidation of *cis*-1,4-polyisoprene on the initial concentration of antioxidants (80 °C, oxygen pressure 10^5 Pa): *1*) 1,3,5-trimethyl-2,4,6-tri(3,5-di-t-butyl-4-hydroxybenzyl)benzene; *2*) ester of 3,5-di-t-butyl-4-hydroxyphenylpropionic acid and pentaerythritol; *3*) 2,2-methylenebis(6-t-butyl-4-methylphenol); *4*) 4,4-methylenebis(2,6-di-t-butylphenol).

Figs.10 and 11 present the variation of the induction period of the oxidation reaction with the initial concentration of the antioxidants and of the inhibited oxidation chain length ν with the reciprocal of the concentration of the antioxidants.

In the concentration range from 4.5×10^{-3} to 4.5×10^{-2} mol kg^{-1} the rate of oxidation is[38]

$$W_{O_2} = \frac{aW_0}{[InH]_0} + bW_0, \quad (5)$$

where a and b are coefficients. The first term of Eqn.(5) reflects the occurrence of a chain oxidation process with chain propagation via the reaction of RO_2 and RH; the second term is associated with the involvement of the inhibitor radicals in chain propagation.

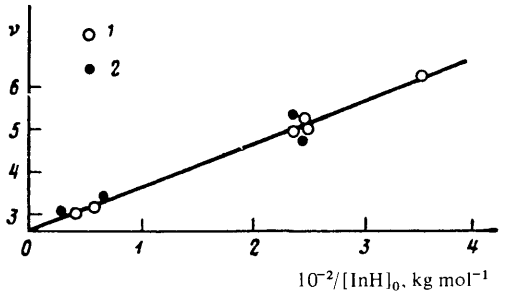
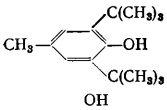
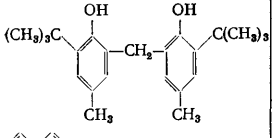
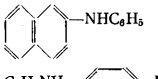
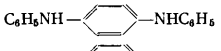
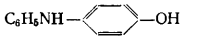
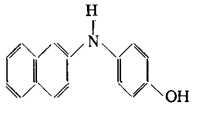


Figure 11. Dependence of the chain length ν of the inhibited oxidation of *cis*-1,4-polyisoprene on the reciprocal of the concentration of antioxidants (80 °C, oxygen pressure 10^5 Pa): *1*) 2,6-di-t-butyl-4-methylphenol; *2*) 2,2-methylenebis(6-t-butyl-4-methylphenol).

Table 3. Kinetic characteristics of the inhibitors of the oxidation and degradation of *cis*-1,4-polyisoprene (80 °C, $p_{O_2} = 10^5$ Pa).

Inhibitor	$k_7 k_6^{-1/2}$, kg$^{1/2}$ mol$^{-1/2}$ s$^{-1/2}$	$10^{-3} \frac{W_{degr}[InH]_0}{W_0^2}$, s
	43	5.5
	36	2.5
	52	2.1
	333	0.27
	3.9	1.4
	4.4	1.4

The rate of degradation of *cis*-1,4-polyisoprene depends on the rate of initiation and on the initial antioxidant concentration:

$$W_{degr} = k_{degr} \frac{cW_0^2}{fk_7[InH]_0}, \quad (6)$$

where k_{degr} is the degradation rate constant and c is a coefficient.

The coefficient of the proportionality between W_{degr} and $W_0^2/[InH]_0$ is a measure of the inhibition of the degradation process by the antioxidant. There is no parallel variation of $k_7(RO_2 + InH)$ and $W_{degr}[InH]_0/W_0^2$. Thus, in order to be able to select effective stabilisers it is important to know their ability to terminate kinetic chains and to suppress oxidative degradation.

Table 3 presents the kinetic characteristics of inhibitors of the phenolic and amine types in the oxidation and degradation of *cis*-1,4-polyisoprene.

Thermoanalytical methods [differential scanning calorimetry (DSC), differential thermal analysis (DTA), and thermogravimetric analysis (TCA)] have been used successfully in recent years for the determination of the efficiency of the action of stabilisers in elastomers.[41]

The thermo-oxidative stability of rubbers containing identical amounts of different antioxidants is estimated in terms of two parameters: the time corresponding to the appearance of the exothermic oxidation peak under isothermal conditions (the induction period τ) and the temperature at which this peak appears in the course of dynamic heating (T_0).

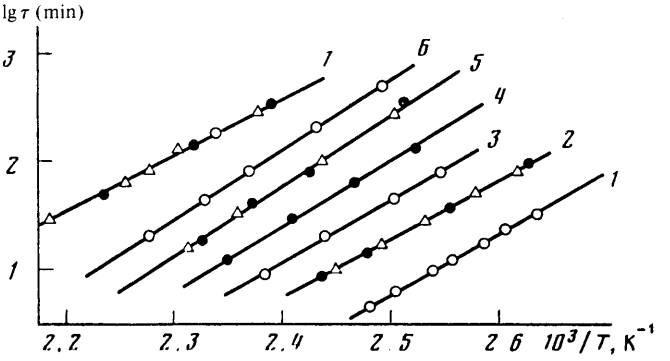


Figure 12. Relation between lg τ and $1/T$ for different compositions: *1*) polyisoprene; *2*) purified natural rubber (NR), NR + 2,6-di-t-butyl-*m*-cresol; *3*) NR + 1,7,10,16-tetrahydroxy-4,13-diazacyclo-octadecane; *4*) NR + *N*-phenyl-β-naphthylamine; *5*) NR + *N*-isopropyl-*N*-phenyl-*p*-phenylenediamine, NR + zinc diethyldithiocarbamate; *6*) raw NR; *7*) NR + *NN'*-diphenyl-*p*-phenylenediamine, NR + *p*-(*p*-toluenesulphanilamido)diphenylamine.

Fig.12 illustrates the linear relations between lg τ and the reciprocal of temperature, the straight lines obtained for different specimens being almost parallel. Analogous results have been obtained in another study.[42] A generalised lg τ – $1/(T + \Delta T)$ relation, where ΔT is a factor defined as the temperature difference $T_{st} - T_{sp}$, was derived from these data (Fig.13). The observed relations give rise to extensive possibilities not only for the estimation of the efficiency of the action of stabilisers but also for predicting the useful life of polymeric articles.

IV. PHOTO-OXIDATIVE AGEING OF ELASTOMERS

1. The Mechanism of Photo-oxidative Ageing

The photochemical oxidation of elastomers is a free-radical chain process with degenerate photobranching by hydroperoxides. This is confirmed by the form of the kinetic curve for the accumulation of the reaction products (ketones and alcohols), which are S-shaped, while the curve describing the variation of the concentration of the hydroperoxy-groups passes through an extremum, the maximum concentration of the hydroperoxides corresponding to the maximum rate of accumulation of the oxidation products (Fig.14).

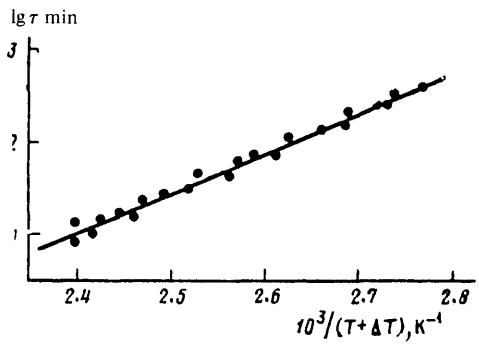


Figure 13. Generalised relation between lg τ and $1/(T + \Delta T)$, where $\Delta T = T_{st} - T_{sp}$ is the difference between the temperatures of the beginning of the exothermic peak for the standard and the specimen.

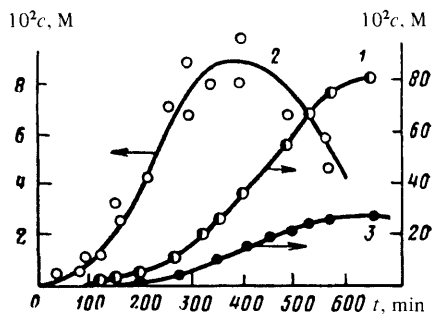


Figure 14. Kinetic curves for the accumulation of hydroxy-groups (curve *1*), carbonyl groups (curve *2*), and hydroperoxy-groups (curve *3*) on irradiation of 0.1 mm polyisoprene films with light having a wavelength $\lambda = 300$ nm.

The termination of the kinetic chain may be quadratic (for example, in polybutadiene) or linear (for example, in polyisoprene). This is manifested by the different character of the dependence of the rate of oxidation on the intensity of light (Fig.15). The chain length in the oxidation of polyisoprene is almost independent of the light intensity and amounts to ~100 units, whereas a decrease in the rate of initiation in polybutadiene, for example from 8×10^{-7} to 8×10^{-9} mol kg^{-1} s^{-1}, increases the chain length from 100 to 1000 units.[43]

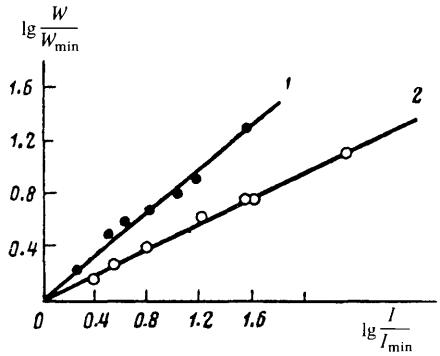


Figure 15. Dependence of the rate of oxidation on the light intensity I in the sensitised photochemical oxidation of polyisoprene (line *1*) and polybutadiene (line *2*); W_{min} and I_{min} are the minimum rate and intensity.

The linear chain termination in certain rubbers indicates that peroxy-radicals decompose with formation of low-molecular-weight radicals. In contrast to the widely familiar oxidation mechanism according to which chain termination takes place on direct interaction of macroradicals, in this case the mechanism is

$$\mathrm{RH} \xrightarrow{W_0/h\nu} \dot{\mathrm{R}},$$
$$\dot{\mathrm{R}} + \mathrm{O_2} \xrightarrow{k_1} \mathrm{R\dot{O}_2},$$
$$\mathrm{R\dot{O}_2} + \mathrm{RH} \xrightarrow{k_2} \mathrm{ROOH} + \dot{\mathrm{R}},$$
$$\mathrm{R\dot{O}_2} \xrightarrow{k_{3.1}} \dot{r},$$
$$\mathrm{R\dot{O}_2} + \dot{r} \xrightarrow{k_{3.2}} \text{products},$$

where $\dot{r}$ is a low-molecular-weight radical. The expression for the rate of oxidation is

$$W = -\frac{d[O_2]}{dt} = \frac{d[ROOH]}{dt} = \frac{k_2[RH]}{k_{3.1}} W_0. \qquad (7)$$

In the general case, the dependence of the rates of oxidation on the rate of initiation (i.e. on the intensity of light) is complex, since at higher rates of initiation direct reactions of the macroradicals, leading to the appearance of a relation of the type $W \sim W_0^{1/2}$, compete with the radical decomposition process leading to linear chain termination. A change in the dependence of the rate of oxidation on the rate of initiation is observed, for example, in the photochemical oxidation of block and statistical butadiene–styrene copolymers.[44]

At room temperature the free radicals formed in the photochemical oxidation of polydienes are relatively unstable and the kinetics of their reaction have therefore been investigated at low temperatures.[45] Irradiation of raw rubbers with ultraviolet light leads to the appearance of EPR signals with a weak resolution (Fig.16), which have been attributed to terminal allyl radicals. On heating, they can be converted into allyl radicals and, in the presence of oxygen, into peroxy-radicals.[46]

The direct study of the nature of the radicals and of the kinetics of their reaction under conditions of photochemical oxidation showed that allyl radicals are the main free-radical species detected by EPR (Fig.17). The free valence in polybutadiene is destroyed on recombination of allyl and not peroxy-radicals, as usually happens in the oxidation of saturated polymers.[47] This feature must be taken into account when the stabilisation of elastomers is considered.

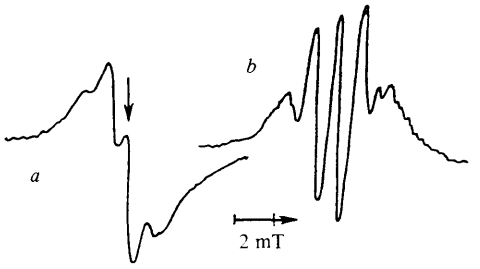


Figure 16. EPR spectra of *cis*-polybutadiene irradiated with ultraviolet light at 77 K: *a*) first derivative; *b*) second derivative; the arrow indicates the position of the DPPH signal.

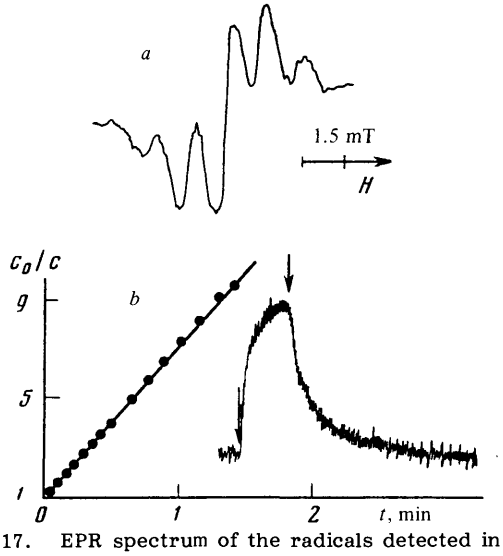
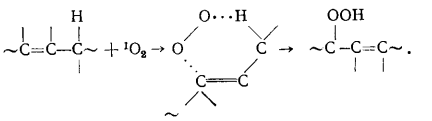


Figure 17. EPR spectrum of the radicals detected in the sensitised oxidation of polybutadiene (*a*) and the kinetics of their accumulation and destruction on switching on and switching off light (*b*); the instants when light is switched on and off are indicated by arrows.

The sensitised oxidation mechanism involving singlet oxygen ($^1O_2$, state $^1\Delta_g$), which has been discussed by a number of investigators[48] and which is an alternative to the free-radical mechanism examined above, proved to be ineffective. The widely current hypothesis of the key role of singlet oxygen in polymer photochemical oxidation processes is based on the postulate of a high reactivity of the double bond towards singlet oxygen in solutions:[49]



However, in elastomers the reactivity of double bonds proved to be much lower (by a factor of 10^2–10^3).[50] This is the main reason why the pathway involving $^1O_2$ cannot compete with the radical chain mechanism for the oxidation of materials based on polydienes.

2. Stabilisation of Elastomers to the Action of Light

The following main mechanisms of the action of photostabilisers of polymeric materials have now been established: (a) shielding (ability to absorb ultraviolet light); (b) quenching of the excited state of the polymer or additives; (c) deactivation of impurities; (d) decomposition of hydroperoxides; (e) interaction with free radicals.

The experimental data concerning the action of stabilisers in polydienes show that the most effective photostabilisers are photoresistant antioxidants (Table 4). Shielding also plays an important role.

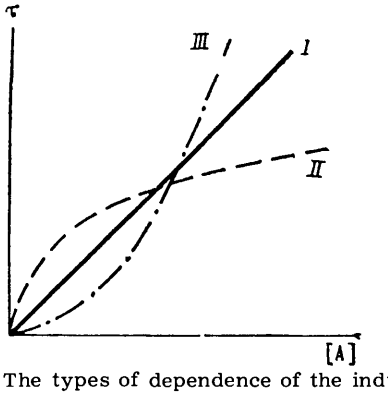


Figure 18. The types of dependence of the induction periods in the photochemical oxidation of elastomers on the concentration of photostabilisers [A].

As a result of the predominance of these two mechanisms, three types of concentration dependences of the induction periods in the photochemical oxidation of elastomers are characteristic of the majority of photostabilisers which are most effective for polydienes (Fig.18). In conformity with the theory of critical phenomena, in the inhibited oxidation[51] of the first type (Fig.18, curve *1*), a nearly linear variation of the induction period τ with the stabiliser concentration [A] is observed when the parameter k_{ROOH}/W_0, characterising the ratio of the rates of degenerate branching and initiation by impurities, does not exceed 10^7 litre mol^{-1}. Such variation is in fact characteristic of the relatively

photoresistant, weakly absorbing antioxidants of the class of stable nitroxy-radicals in polydienes (Fig.19) as a consequence of the high value of W_0.

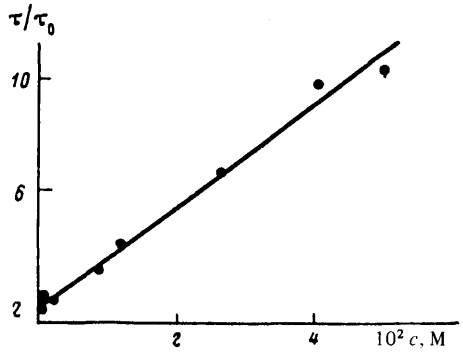


Figure 19. Dependence of the induction period in the photochemical oxidation of DSSK-30 butadiene–styrene rubber on the concentration of the 4-benzoyloxy-2,2,6,6-tetramethylpiperidin-1-yloxy-radical.

A second type of dependence of τ on [A] (with saturation, curve II in Fig.18) is observed when the stabiliser is photochemically unstable and can initiate photochemical oxidation:

$$\mathrm{RH} \xrightarrow{h\nu;\ W_0} \dot{\mathrm{R}},$$
$$\dot{\mathrm{R}} + \mathrm{O_2} \xrightarrow{k_1} \mathrm{R\dot{O}_2},$$
$$\mathrm{R\dot{O}_2} + \mathrm{RH} \xrightarrow{k_2} \mathrm{ROOH} + \dot{\mathrm{R}},$$
$$\mathrm{A} + f\mathrm{R\dot{O}_2} \xrightarrow{k_4} \text{products},$$
$$\mathrm{A} + \mathrm{RH} \xrightarrow[\mathrm{O_2}]{h\nu;\ k_5} \mathrm{R\dot{O}_2}.$$

In this case

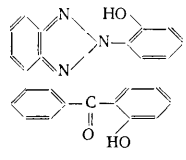
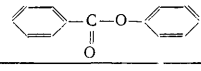
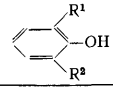
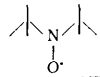
$$\tau = \frac{1}{k_5\,(1 + m/f)} \ln\left\{1 + \frac{k_5\,(1 + m/f)\,[\mathrm{A}]}{W_0}\right\}, \qquad (8)$$

where m is the number of radicals formed from the stabiliser A and f is the inhibition coefficient. An example of such a relation is presented in Fig.20.

A third type of such variation, to which curve III in Fig.18 corresponds, is characteristic of the case where the same substance behaves both as the antioxidant and as the absorber of ultraviolet light. The concentration variation of τ is described by the equation

$$\tau = \frac{2.3f\,[\mathrm{A}]^2\varepsilon l}{W_0}, \qquad (9)$$

Table 4. Mechanisms of the photoprotective action of stabilisers.

Type of stabiliser	Main fragment	Effectiveness in polydienes	Main mechanism	Additional mechanism	Factor limiting effectiveness
Benzotriazoles and benzophenones		Low	Quenching	Shielding (large thicknesses)	—
Phenyl benzoates and phenyl salicylates		Low	Rearrangement to benzoates	Shielding (large thicknesses)	—
Aromatic amines	Ar—NH—Ar	Low	Interaction	—	Photostability
Sterically hindered phenols		Moderate	Interaction with radicals	—	Photostability
Sterically hindered amines		High	Oxidation with formation of inhibitors	—	Photostability of nitroxy-radicals
Stable nitroxy-radicals		High	Interaction with radicals	—	Photostability
Metal complexes (with dialkyldithiocarbamates)	ML_n, where $L = R_2N—\overset{\overset{S}{\|}}{C}—S—$	Moderate	Decomposition of hydroperoxides	Interaction with radicals; shielding	Low photostability
Azophenols and azoamines	Ar—N=N—Ar—X, where X=OH, NH_2	High	Interaction with radicals	Shielding (large thicknesses)	Low photostability

where ε is the extinction coefficient and l the thickness of the polymer film. The experimental curve corresponding to this type is illustrated in Fig.21.

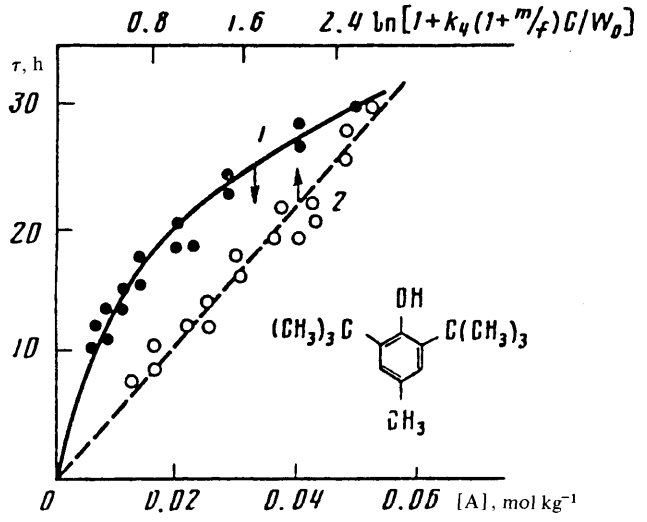


Figure 20. Dependence of the induction period in the photochemical oxidation of a film of IST-30 butadiene–styrene block copolymer on the concentration of 2,6-di-t-butyl-4-methylphenol (curve *1*) and its linear form in terms of the variables of Eqn.(8) (line *2*).

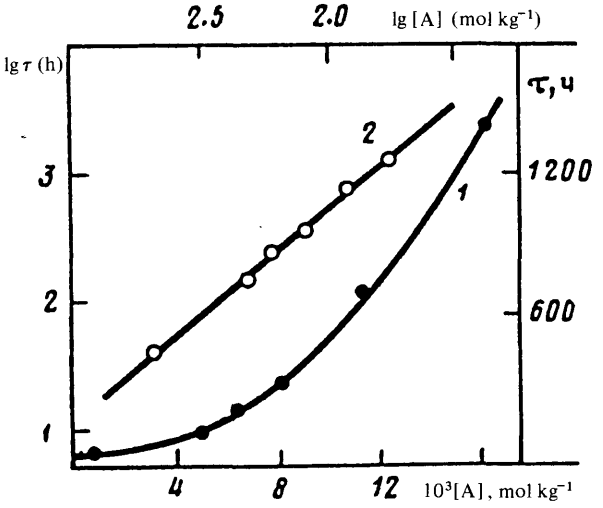
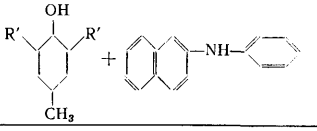
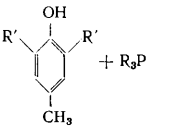
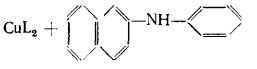
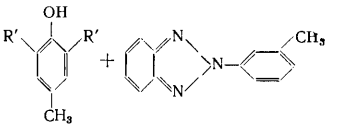
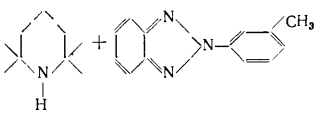


Figure 21. Dependence of the induction period in the photochemical oxidation of a film of the IST-30 butadiene–styrene block coploymer on the concentration of 4-hydroxy-3-methylphenylazo(azobenzene) (line *1*) and its logarithmic form (line *2*).

(a) *Synergism in the stabilisation of polymers towards the action of light.* Synergistic mixtures of stabilisers, whose classification as well as that of the mechanism of the synergism are given in Table 5, are widely used in practice for the stabilisation both of elastomers and of other polymeric materials.[52–57]

Table 5. The principal mechanism of the action of synergistic systems.

Mechanism	General mechanism of action of system	Example of system
	Thermal oxidation	
Regeneration of active inhibitor	$A^1 \rightleftharpoons \dot{R}$ (+A^2)	
Decrease of critical inhibitor concentration	$RO_2 + RH \rightarrow ROOH + \dot{R}$ $ROOH \rightarrow \dot{R}O_2$ $\dot{R}O_2 + A^1 \rightarrow$ products $ROOH + A^2 \rightarrow$ products (Tbl)	
Formation of new stabiliser	$A^1 + A^2 \rightarrow A^3$	
	Photochemical oxidation	
Quenching of excited states of antioxidant	$A \rightleftharpoons A^* \rightarrow$ products (Q)	
Diffusion of antioxidant from the volume protected by the u.v. ligh absorber to the surface layer undergoing photochemical oxidation	$[A]_{eff} = [A]_{av} L/l$	

Notation: L = thickness of specimen, l = thickness of surface layer, A* = excited state of photostabiliser, Q = quenching agent, and R′ = $C(CH_3)_3$.

In the photochemical oxidation of polymers systems acting according to two fundamental principles are capable of exhibiting synergism: with and without the interaction of the components. Among the possible mechanisms, the principal ones are the physical mechanisms involving the quenching of excited states of the antioxidants, the diffusion of the antioxidant from the volume protected by the ultraviolet light absorber to the surface layer undergoing oxidation, and the influence of additives on the distribution of stabilisers in polymers.

The diffusion mechanism of the synergism was analysed quantitatively for an antioxidant which does not absorb light and a strongly absorbing ultraviolet light absorber, both uniformly distributed throughout the thickness of the specimen.[55] The light intensity in the polymer film decreases as one moves away from the irradiated surface in proportion to $\exp(-\varepsilon c x)$, where x is the distance from the surface and c the concentration. The rate of photochemical processes varies in accordance with the same law within the thickness of the specimen and one can assume

that photoprocesses proceed mainly in a narrow surface zone whose width is $1/\varepsilon c$. The antioxidant present in the polymer is consumed in this zone at a much higher rate than in the deeper layers. The concentration gradient thus generated leads to the appearance of a diffusional flux of the antioxidant from the bulk of the specimen to the surface layer, the flux decreasing the rate of the photoprocess in the reaction zone, while the deep layers of the specimen serve as a "reservoir" of the antioxidant.

For an oxidation process described by the general scheme

$$\mathrm{RH} \xrightarrow{O_2;\ W_0} \mathrm{R\dot{O}_2},$$
$$\mathrm{R\dot{O}_2} + \mathrm{RH} \xrightarrow{k_1} \mathrm{ROOH} + \dot{\mathrm{R}},$$
$$\mathrm{R\dot{O}_2} + \mathrm{R\dot{O}_2} \xrightarrow{k_2} \text{products},$$
$$\mathrm{R\dot{O}_2} + \mathrm{A} \xrightarrow{k_3} \text{products},$$
$$\mathrm{ROOH} + \mathrm{A} \xrightarrow{k_4} \text{products},$$

the following system of equations has been obtained taking into account the diffusion of the antioxidant into the zone where oxidation takes place:

$$\frac{\partial [\mathrm{R\dot{O}_2}]}{\partial t} = W_0 \exp(-\varepsilon c x) - f_b k_3 [\mathrm{R\dot{O}_2}][\mathrm{A}] - 2k_2 [\mathrm{R\dot{O}_2}], \qquad (10)$$

$$\frac{\partial [\mathrm{A}]}{\partial t} = -k_4 [\mathrm{ROOH}][\mathrm{A}] - f_b k_3 [\mathrm{R\dot{O}_2}][\mathrm{A}] - \frac{\partial^2 [\mathrm{A}]}{\partial x^2} D, \qquad (11)$$

$$\frac{\partial [\mathrm{ROOH}]}{\partial t} = k_1 [\mathrm{RH}][\mathrm{R\dot{O}_2}] - f_h k_4 [\mathrm{ROOH}][\mathrm{A}], \qquad (12)$$

subject to the initial conditions

$$[\mathrm{A}]_{t=0} = [\mathrm{A}]_0;\ [\mathrm{R\dot{O}_2}]_{t=0} = 0;\ [\mathrm{ROOH}]_{t=0} = 0$$

and the boundary conditions

$$\left.\frac{\partial [\mathrm{A}]}{\partial x}\right|_{\substack{x=0,\\ x=l}} = 0;\ \left.\frac{\partial [\mathrm{R\dot{O}_2}]}{\partial x}\right|_{\substack{x=0,\\ x=l}} = 0;\ \left.\frac{\partial [\mathrm{ROOH}]}{\partial x}\right|_{\substack{x=0,\\ x=l}} = 0,$$

where l is the thickness of the film, D the diffusion coefficient of the antioxidant, ε and c are the extinction coefficient and the concentration of the ultraviolet light absorber, and f_b and f_h are the branching and inhibition coefficients.

The system in a general form can be solved numerically and, subject to a number of physically justified simplifying assumptions, also analytically. Two typical cases are of the greatest interest from the practical point of view.

1. Rapid diffusion regime, where the concentration of A is almost constant throughout the thickness of the specimen. For strongly absorbing specimens and when substances A reacting with free radicals are employed, we have

$$\tau = \left\{\frac{([\mathrm{A}]_0 - [\mathrm{A}])}{W_0}\right\} f_b \varepsilon c l. \qquad (13)$$

In the case of compounds A which react with peroxides, we obtain

$$\tau = \left\{\frac{([\mathrm{A}]_0 - [\mathrm{A}])}{(k_2 [\mathrm{RH}])}\right\} f_h \varepsilon c l \left(\frac{2k_3}{W_0}\right)^{1/2}. \qquad (14)$$

2. Diffusion-controlled regime. Diffusion results in an additional supply of the antioxidant to the surface layer, but this does not equalise the concentration of A throughout the thickness of the specimen. The corresponding expressions for τ assume the following form:

$$\tau = \pi D \{f_b \varepsilon c ([\mathrm{A}]_0 - [\mathrm{A}])/2W_0\}^2; \qquad (15)$$

$$\tau = [2\pi D k_3/W_0]\{f_h \varepsilon c ([\mathrm{A}]_0 - [\mathrm{A}])/(2k_3[\mathrm{RH}])\}^2. \qquad (16)$$

It follows from theoretical relations that the photostability of the specimen depends on the overall concentration of stabilisers, the component ratio (the 1:1 ratio is optimum), the thickness of the specimen, and, in the diffusion-controlled regime, also the light intensity. These relations have been tested experimentally. The results presented in Fig.22 show that there is a satisfactory agreement between theory and experiment.

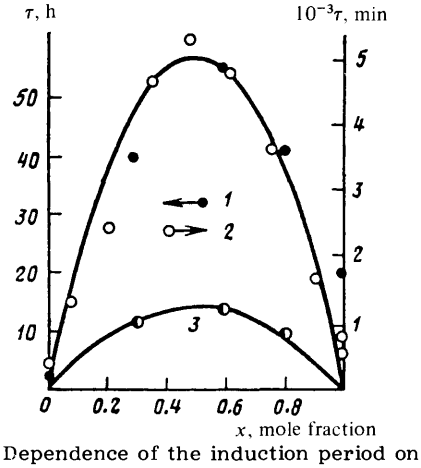


Figure 22. Dependence of the induction period on the mole fraction of the antioxidant in the photochemical oxidation of 60 μm (curve *1*) and 10 μm (curve *3*) polybutadiene films containing a mixture of 4-heptyloxy-2-hydroxybenzophenone and 2,6-di-t-butyl-4-methylphenol as well as films of polychloropropene containing a mixture of 2-hydroxy-4-octyloxybenzophenone and bis(3-t-butyl-2-hydroxy-5-methylphenyl)methane (curve *2*).

(b) *Synergism in the quenching of the excited states of the antioxidants by photostabilisers.* If the antioxidant is photochemically active, then synergism is possible when a photostabiliser capable of deactivating the excited states of the antioxidant is used as a second component. In the presence of a mixture of a quenching agent Q and an antioxidant A, the dependence of the induction period on the concentrations has the following form:

$$\frac{\tau}{\tau_0} = \ln(1 + \beta [\mathrm{A}]\eta)/\eta \ln(1 + \beta [\mathrm{A}]), \qquad (17)$$

where $\beta = k_5(1 + m/f)/W_0$, k_5 is the rate constant for the photochemical reaction of the antioxidant, and $\eta = [\mathrm{A}^*]_Q/[\mathrm{A}^*]$ a coefficient characterising the decrease of the rate constant for photochemical initiation involving A in the presence of Q. Fig.23 presents the dependence of the relative induction period in the photochemical oxidation of polybutadiene films on the relative concentration of the quenching agent, illustrating this mechanism of the synergism.

A new principle for the construction of synergistic systems involving the use of additives influencing the distribution of stabilisers in polymers has been proposed recently on the basis of a detailed study of the solubilities and distribution of additives in polymers. Such additives can be both chemically relatively inert substances (for example,

surfactants) and certain stabilisers. The highest efficiency of the synergistic mixture is then attained when photostabilisers are employed as the additional additives.[57]

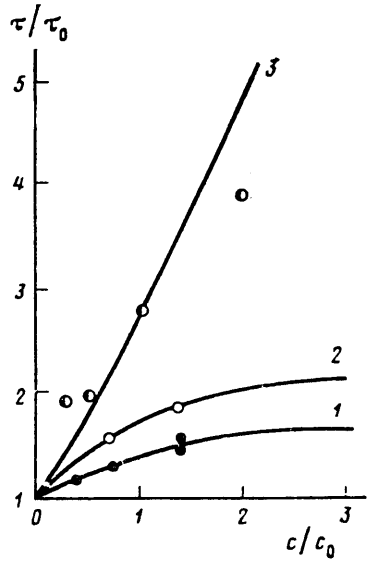


Figure 23. Dependence of the induction period on the concentration of the quenching agent. Curves—theoretical calculations for $\beta[A]_0 = 2$ (curve *1*), 4 (curve *2*), or 20 (curve *3*); circles—experimental data for mixtures of 2-(2-hydroxy-5-methylphenyl)benzotriazole and bis(3-t-butyl-2-hydroxy-5-methylphenyl)methane (curves *1* and *2*) or 2,6-di-t-butyl-4-phenylphenol (curve *3*).

(c) *The influence of the supermolecular structure on the efficiency of photostabilisers.* Thermoelastoplastics have now found extensive applications. These materials occupy an intermediate position, as regards their properties, between plastics and elastomers and consist of block copolymers. When the properties of the block differ appreciably, they form different phases with a fairly sharp interface.[58,59] Such materials include, for example, diene–styrene block copolymers. The kinetics of the photoprocesses are then influenced by the distribution of the stabilisers between the phases and their migration from one phase to another. For diene–styrene block copolymers, the difference between the reactivities of the additives to the "hard" and elastomeric phases is so significant that this property can be used to investigate the distribution and migration of additives.

For example, even after a brief irradiation with ultraviolet light of copolymer specimens containing stable nitroxy-radicals, the latter are almost fully consumed in the polydiene phase, whereas not more than 10% are consumed in the polystyrene phase (Fig.24, *a* and *b*). When the specimen is kept in the dark, the concentration of the nitroxy-radicals in the polystyrene phase falls, while that in the polydiene phase increases (Fig.24c), and after prolonged storage the initial distribution of the additive is restored. These data made it possible to estimate the distribution of the stabiliser between the phases and to determine the diffusion coefficient in the "hard" phase.

The photostability of the copolymer depends on the ratio of the volumes of the "hard" and elastomeric phases. Effective stabilisation requires the use of additives which are predominantly concentrated in the hard phase where they are more resistant to the action of light and hence can diffuse to the elastomeric phase being oxidised, ensuring its photostabilisation. The interfacial diffusion of the stabiliser must also be taken into account in selecting the conditions for accelerated tests of elastomers for photostability.

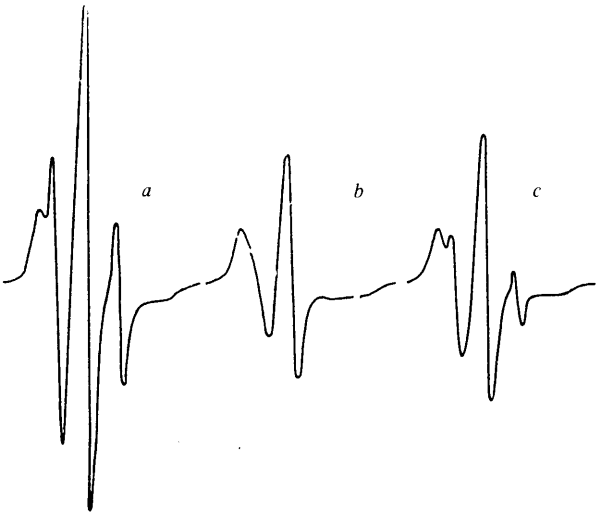


Figure 24. EPR spectra of the 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-yloxy-radical before (*a*) and after (*b*) irradiation with ultraviolet light for 2.5 min and also after maintaining the irradiated specimen in the dark for 100 min (*c*).

V. OZONE-INDUCED AGEING OF ELASTOMERS

Ozone is an active species in the ageing of elastomers containing double bonds in the main chains of the macromolecules. Ozone is formed at sites where electric motors operate, electric welding is carried on, and sources of ultraviolet light are employed. Considerable amounts of corrosive gases, ejected with the exhaust gases of automobiles and with factory smoke, are formed in the air of large cities and industrial undertakings. Photochemical smog, one component of which is ozone, is formed from these gases under special meteorological and geographical conditions. The concentration of ozone in photochemical smog (up to 5×10^{-1} mg m^{-3}) is sufficient for the ageing of the majority of technical rubber articles.[60]

As ozone adds to the macromolecules of the elastomer, the formation and growth of surface cracks and the accumulation of oxygen-containing groups in the surface layer are observed. The absorption of ozone by stretched elastomer specimens differs significantly from that by undeformed specimens.[61] The rate of absorption of ozone by the specimens in the absence of stretching stresses diminishes after several minutes of exposure. The layer formed on the surface, on which the double bonds have reacted,

inhibits further absorption of ozone. The rate of absorption of ozone by stretched specimens remains close to the initial value, since the cracks formed under the influence of mechanical stresses open up and continually regenerate a fresh surface.

1. Kinetics and Mechanism of the Degradation of Polymers by Ozone

When polymers are acted upon by ozone, a decrease of the molecular weight and the accumulation of oxygen-containing functional groups (acids, ketones, peroxides, etc.) are observed.[62] Table 6 presents the effective rate constants for the reactions of ozone with the functional groups and the numbers of breaks in the chain per reaction step (n) in solution in carbon tetrachloride. The following trend has been observed for polymers: with increase in the rate constant for the reaction of ozone with the polymer, the number of breaks per reaction step diminishes.

Table 6. The rate constants for the reactions of ozone with various polymers k_{eff} and the numbers of chain breaks n per reaction step in solution in CCl_4 at 20 °C.[62]

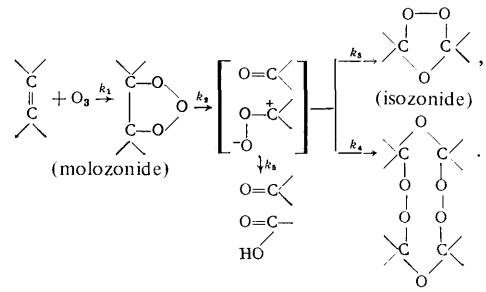
Polymer	k_{eff}, litre mol^{-1} s^{-1}	n
Polyphenyl	$5.0\cdot10^{-2}$	—
Polynaphthalene	$2.0\cdot10^{3}$	—
Polycarbonate	3,0	—
Polyisobutylene	$1.2\cdot10^{-2}$	0.05
Polyethylene	$4.6\cdot10^{-2}$	0.1
Ethylene-propylene copolymer	$6.0\cdot10^{-2}$	0.06
Polypropylene	$8.0\cdot10^{-2}$	0.1
Polystyrene	0,3	0.01
Polyvinylcyclohexane	0,8	—
Polyphenylacetylene	$1.4\cdot10^{3}$	—
Polybutadiene	$6.0\cdot10^{4}$	0.06
Polyisoprene	$4.4\cdot10^{5}$	0.002
Polychloroprene	$1.0\cdot10^{4}$	—

Table 7. The rate constants for the reactions of ozone with elastomers deposited on a fine-grained silica gel at 20 °C.

Elastomer	$10^{-4}\,k_{eff}$, kg mol^{-1} s^{-1}
Natural rubber	10.5
Polyisoprene	10.5
Polybutadiene	5.1
Butadiene-styrene copolymer (SKS-30 ARKP)	4.6
Polychloroprene	1.0
Butyl rubber	10.5

Table 7 presents the rate constants for the reactions of ozone with the elastomers deposited on a fine-grained silica gel in order to eliminate diffusion-dependent limitations. These rate constants are satisfactorily correlated with the rate constants for the corresponding polymers in solution (Fig.25). This makes it possible to predict the resistance of elastomeric materials to ozone with the aid of model experiments carried out in solution.

The degradation of elastomer fragments with unsaturated bonds proceeds via the formation of a molozonide and zwitter-ions in accordance with the scheme



The macromolecules are cleaved only as a result of the reaction with the rate constant k_5; the contribution of this reaction does not exceed 1–2%. The main reaction product is the isozonide.

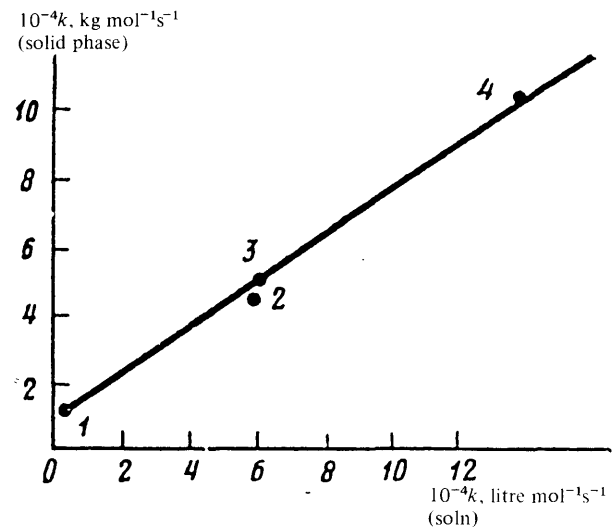


Figure 25. Correlation between the rate constants for the reactions of ozone with polydienes in solution and in the solid phase: *1*) polychloroprene; *2*) butadiene–styrene copolymer; *3*) *cis*-polybutadiene; *4*) *cis*-polyisoprene.

2. Protection of Polymeric Materials Against the Action of Ozone

Antiozonants and wax are used to protect elastomers against the action of ozone. Antiozonants include compounds of two classes: *p*-phenylenediamines and dihydroquinolines. There exist different explanations of the protective action of *p*-phenylenediamines in relation to ozone:

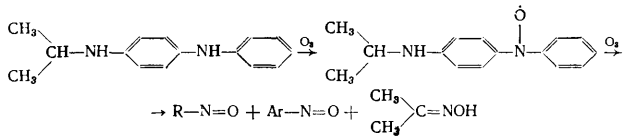
(a) The antiozonant reacts with ozone, diffusing to the surface of the article and forming a protective layer which constitutes a physical barrier.[63] This mechanism does not explain the effectiveness of antiozonants in elastomers subjected to a dynamic load, where the protective layer cannot remain continuous.

(b) The antiozonant reacts with the product of the addition of ozone to the polymer, preventing the decomposition of the resulting ozonides[64-66] or connecting the ends of the ruptured chains.[67,68] This hypothesis has not so far received convincing experimental confirmation.

(c) The antiozonant catalyses the decomposition of ozone on the surface of elastomers. This mechanism is inconsistent with the process kinetics.

(d) The antiozonant is a powerful competitor with the elastomer double bonds in the reaction with ozone. Despite its satisfactory agreement with many experimental data,[69] this mechanism cannot explain why other additives which actively react with ozone are ineffective.[70]

Ozone reacts with *p*-phenylenediamine to form nitroxyradicals, which are further converted into nitrosoalkyls, nitrosoallyls, and oximes:[71]



Dihydroquinones are less reactive than *p*-phenylenediamines but the antiozonants of these classes exhibit synergism in their influence on the resistance to ozone.[72]

Among the explanations of the protective action of antiozonants, the last has received the greatest amount of experimental confirmation: the antiozonant traps ozone on the surface of the elastomer. Fig.26 presents the logarithmic dependence of the relative time before the appearance of cracks on the relative rate constant for the interaction of ozone with the antiozonant in solution in carbon tetrachloride.[69]

The protective action of waxes is based on two effects:[73] the creation of a binary layer on the surface which diminishes the permeability of the polymer to ozone and interaction with ozone. For protective waxes, there is also a correlation between the time before the appearance of cracks and the rate constant for the reaction of ozone with the waxes (Table 8).

Table 8. The rate constants for the reactions of ozone with protective waxes in solution in CCl_4 at 23 °C on the time before the appearance of a crack on the SKI-3 elastomer during atmospheric ageing.[73]

Wax	$10^3 k$, litre $mol^{-1}s^{-1}$	τ, days	
		Batumi	Tashkent
Paraffin	4	30	32
MEV-1	42	54	60
MEV-2	60	180	90
MEV-4	70	100	65
Ceresite-80	6	119	59
MEVu-2	107	687	105

VI. THE INFLUENCE OF MECHANICAL STRESSES ON THE KINETICS OF THE REACTIONS OF ELASTOMERS

The influence of stress on the reactivity of elastomer macromolecules in reactions of various types has been observed and studied quantitatively. The stresses have accelerating, retarding, and neutral effects. The experimental data have been interpreted theoretically from the standpoint of transition state theory and conformational analysis.[74]

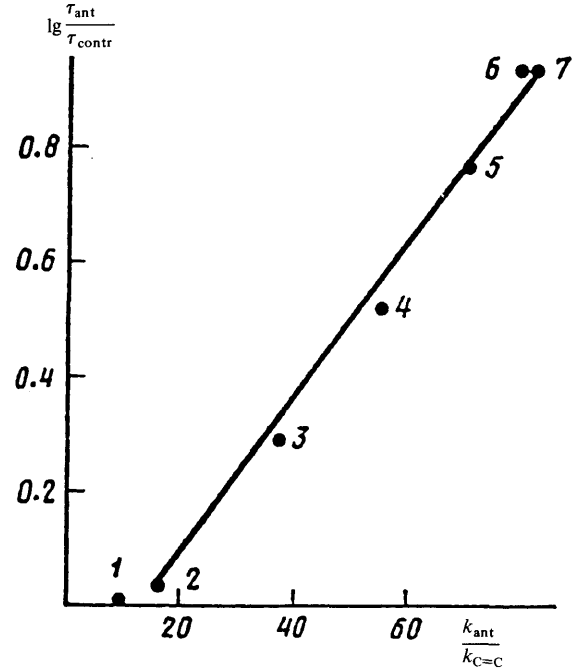
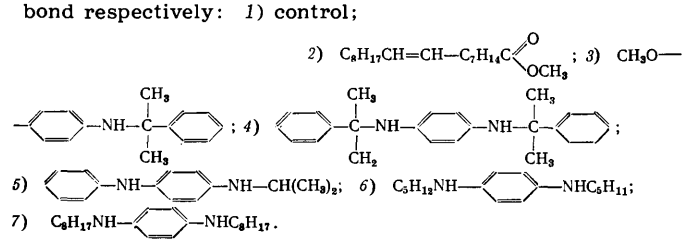


Figure 26. Logarithmic dependence of the optimum time τ_{ant} of the appearance of cracks on the relative rate constant for the interaction of ozone with antiozonants in solution in CCl_4; k_{ant} and $k_{C=C}$ are the rate constants for the reactions of ozone with the antiozonant and the double bond respectively: *1*) control;



In real articles excessive stresses can arise in the region of defects (for example, at the mouth of the crack) and the effects described above are in fact to be expected there.

One of the most dangerous reagents is atmospheric ozone, whose action is accompanied by the formation of microcracks and macrocracks. Fig.27 presents data concerning the influence of stretching stresses and deformations on the rate of growth of cracks, the lifespan, the degree of oxidation, and the chemical relaxation time of the elastomers. With increased load, the above parameters are found to increase in the initial stage up to ~20% deformation. After that, the degradation process slows down—the resistance to ozone-induced ageing increases with increasing stretching stress. This constitutes the fundamental difference from the familiar

dependence of the life of polymers on the load—an exponential decrease of the lifespan with increasing σ (Zhurkov's equation).

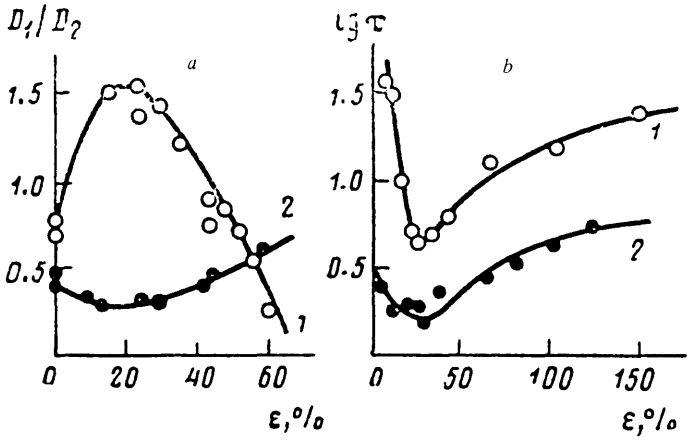
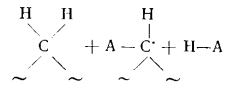


Figure 27. Variation of the optical density ratios D_{1720}/D_{1640} (curve *1*) and D_{1640}/D_{1375} (curve *2*) with the degree of deformation of *cis*-polyisoprene in its reaction with ozone; $[O_3] = 7 \times 10^{-8}$ M, 20 °C; *b*) variation of the chemical relaxation time of *cis*-polyisoprene with the degree of deformation in an atmosphere of ozone: *1*) $[O_3] = 2 \times 10^{-6}$ M; *2*) $[O_3] = 1 \times 10^{-5}$ M, 20 °C.

The phenomenon of "critical" deformation can be accounted for by a change of the reactivity of the double bond. This effect is caused by the competition of two opposed processes: the formation of cracks, which accelerate degradation, and a decreased reactivity of the double bond at the mouth of the crack. The first factor is manifested even for the smallest deformations. The contribution of the second is possible only when breaking stresses appear and therefore the first and second factors predominate respectively under the conditions of small and large deformations.[74]

The critical deformation is manifested most strikingly in elastomers with a *cis*-structure; in natural rubber and its synthetic analogue—polyisoprene as well as polybutadiene. In all these cases the stretching deformations do not increase the hardness of the elastomers and it is therefore impossible to account for the decreased rate of oxidative degradation with increasing deformation by a change in physical properties. The retarding influence of the physical factor can be shown only in systems where the molecular mobility diminishes with increasing stretch, as happens, for example, in the butadiene–styrene rubber with a *trans*-structure; however, the critical deformation in such systems is much less pronounced. This is apparently caused mainly by the fact that they have a *trans*-configuration of the monomer units, the reactivity of whose double bonds does not diminish under the influence of loads.

Many reactions of elastomers are accompanied by the rehybridisation of the carbon atoms in the main chain from the sp^2 to the sp^3 state. These can be both free-radical processes and reactions proceeding via S_N1 and S_N2 mechanisms. One of the commonest processes of this type is the abstraction of a hydrogen atom:



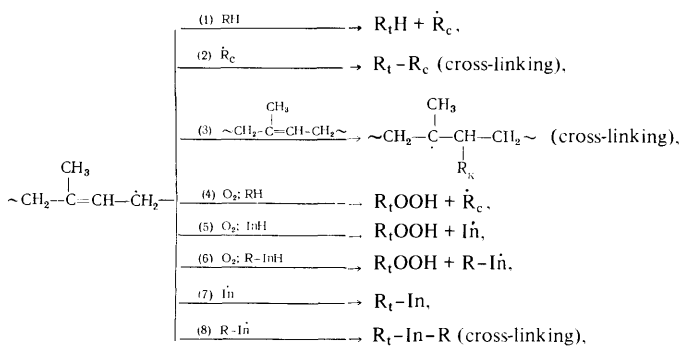
where A is a hydrogen acceptor (a molecule, a radical, or an atom, for example, O_3, O_2, RO_2, HO, CCl_3, Cl, Br, stable nitroxy-radicals, etc.). This reaction is extremely important in the thermo-oxidative degradation of elastomers (initiation, chain propagation, etc.). Recent studies have shown that the rates of reactions of the above class increase under the influence of external stretching stresses. A universal equation relating the rate of reaction to the load and temperature has been obtained:[74]

$$\ln\left(\frac{v_\sigma}{v_0}\right) = \frac{\alpha\sigma}{RT}, \qquad (18)$$

where v is the rate of reaction, the subscripts σ and 0 refer to a polymer specimen with a load and without a load respectively, σ is the stress, and α a proportionality coefficient, which depends on the nature of the acceptor and the supermolecular structure of the specimen.

VII. THE ROLE OF RADICAL REACTIONS IN THE WEAR OF VULCANISED ELASTOMERS

Antioxidants exert a significant influence on the rate of wear of vulcanised elastomers with polysulphide cross-links under "rolling-up" conditions, low-molecular-weight antioxidants increasing the rate of the process and those linked to the network decreasing it.[75] These data can be accounted for by the following reaction scheme for the terminal macroradicals arising as a result of mechanical breaks in the vulcanisation network in the region of the rupture centre, which is produced when a strip is torn off and twisted in the "net".



where R_t and R_c are the terminal and central radicals respectively.

Reactions (2), (3), and (8) lead to the formation of new cross-links and thereby heal the network defects, which is the cause of the retardation of wear in the absence of low-molecular-weight antioxidants.

In the presence of low-molecular-weight antioxidants the terminal macroradicals in the region of the growing decomposition centre are stabilised in the reactions with the antioxidants and thereby prevent the processes leading to the healing of the network defects.[75]

The problem of the ageing and stabilisation of elastomers constitutes a major branch of polymer materials science—the science concerned with the creation of polymeric materials

and the preservation or regulation of their physical properties. Chemical processes alter the structure and physical properties of polymers, while the structural–physical properties of the polymer strongly influence in their turn the direction and rate of its chemical reactions.

Thus the physicochemical approach to problems of polymer materials science is best adapted to the specific features of this field, being concerned with a combination of the problems of the physics and chemistry of elastomeric materials, and creating new ways and principles for the control of their properties and stability.

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Reactive Derivatives of Nucleic Acids and Their Components as Affinity Reagents

D.G.Knorre and V.V.Vlasov

The review is devoted to derivatives of nucleic acids and their components—nuclectides, nucleoside triphosphates, and oligonucleotides carrying reactive groups. Such derivatives are important tools for the investigation of protein-nucleic acid interactions and the functional topography of complex protein and nucleoprotein structures and can give rise to the prospect of being able to influence in a highly selective manner living organisms, including the nucleic acids and the nucleoproteins of the genetic apparatus. The review considers the principal groups of such reagents, the methods of their synthesis, and their properties which determine the possibility of their use for the selective (affinity) modification of biopolymers. The general principles of the construction of affinity reagents and their applications are analysed in relation to nucleotide affinity reagents. The bibliography includes 121 references.

CONTENTS

I. Introduction 836
II. Certain physicochemical characteristics of the affinity modification process 837
III. The principal problems solved by the method of affinity modification and the general principles governing the construction and use of affinity reagents 839
IV. Reactive derivatives of nucleosides and nucleoside mono-, di-, and tri-phosphates 843
V. Reactive derivatives of oligonucleotides 846
VI. Reactive derivatives of nucleic acids 847

I. INTRODUCTION

Among the inexhaustible variety of proteins in living nature, a large group of proteins possess the ability to interact specifically with nucleotides and nucleic acids having a definite structure. The substrates or effectors for hundreds of enzymes with different specificities are nucleotides, nucleoside di- and tri-phosphates, and nucleotide coenzymes. Virtually all the proteins and the nucleoproteins ensuring the storage, replication, and application of hereditary information in cells and viruses participate in selective interaction with nucleic acids. These are the enzymes of the DNA replication system, enzymes for the transcription and subsequent processing of the RNA formed, the repair enzymes ensuring the removal of damaged sections of DNA and their regeneration, and all the macromolecular components involved in the biosynthesis of proteins, including aminoacyl-tRNA-synthetases, ribosomes, and numerous translation factors. The study of the mechanism and, in the first place, the structural principles of the selective interaction of nucleic acids and nucleotides with proteins, frequently referred to as the protein–nucleic acid recognition, is one of the essential tasks of molecular biology and bio-organic chemistry.

The selective interaction between nucleic acids is of no less cardinal importance, although perhaps not in terms of quite so many aspects, in ensuring the operation of the key processes involved in vital activity. It is sufficient to recall that the specific interaction of the complementary nucleotide sequences constitutes the basis of the double helix structure of DNA established by Watson and Crick.[1]

One of the most effective methods for the study of the specific interactions of biopolymers with low-molecular-weight or polymeric partners (ligands) is chemical modification of biopolymers by means of reagents which retain the principal structural features of a specific ligand and hence the affinity for the polymer and at the same time carry a reactive group capable of chemical interaction with the biopolymer under conditions close to those which really obtain in its functioning. Such reagents have been called affinity reagents and the method itself is usually referred to as affinity labelling or affinity modification.[2,3] In the complex of a biopolymer with an affinity reagent the chemical reaction with the biopolymer takes place in the vicinity of the region of specific interaction (recognition), the ligand being covalently fixed in this region. The fragment of the affinity reagent ensuring a specific affinity for the biopolymer directs the reagent to a specific section on the surface of the protein molecule or to a specific sequence of nucleotides in the nucleic acid and therefore constitutes a kind of address which helps the reacting group to find its target. Affinity reagents can therefore be referred to also as addressed reagents.

Reactive derivatives of nucleic acids and their components are therefore important instruments for the investigation of the protein–nucleic acid recognition and the interaction between nucleic acids. These derivatives also lead to the prospect of being able to act in a highly selective manner on many key biochemical and molecular-genetic processes in living organisms.

This review is devoted to the chemistry of addressed nucleotide reagents, containing as the address nucleotides, nucleoside triphosphates, oligonucleotides, and nucleic acids, the methods of their synthesis, and their properties important for their use in affinity modification. Its aim is not to give a systematic account of all the numerous applications of the reagents for the solution of problems in biochemistry, molecular and cell biology, and medicine. These applications constitute merely individual, most thoroughly demonstrated and important examples. To a large extent the review is based on the studies carried out in the Biochemical Division of the Novosibirsk Institute of Organic Chemistry, Siberian Division of the USSR Academy of Sciences, which has now been transformed into the Novosibirsk Institute of Bio-organic Chemistry.

Reactive derivatives of nucleic acids and their components constitute one of the most systematically investigated groups of affinity reagents. The main principles of their construction, the problems arising in the use of such derivatives, and the ways in which they can be solved have therefore been elucidated in a particularly clear-cut manner in the course of their investigation. A special Section of the review is therefore devoted to the general questions of affinity modification in relation to addressed nucleotide reagents.

II. CERTAIN PHYSICOCHEMICAL CHARACTERISTICS OF THE AFFINITY MODIFICATION PROCESS

According to the main idea of the method of affinity modification, the reaction of a biopolymer P proceeds in a complex with an affinity reagent attached via a system of non-covalent interactions in the region where the biopolymer recognises a certain natural ligand L. The formation of the complex PL can be detected either by a number of physicochemical methods or from the manifestation of the biological function due to the interaction of P with L. In most of the examples below we are dealing with enzyme activity, a quantitative characteristic of which is the rate of the enzyme-catalysed reaction. This rate is proportional to the concentration of the enzyme–substrate complex or, in the case of a reaction involving two substrates, the concentration of the complex of the enzyme with both substrates. The recognition region is in this case part of the active centre of the enzyme.

The concentration of the complex PL is given by

$$[PL]=K[L]P_t/(1+K[L]),$$

where K is the constant for the association of P with L and P_t the total concentration of the biopolymer.

The affinity reagent, constructed on the basis of a natural ligand L and containing a reactive group X, can be represented by L–X. This reagent competes with L for the recognition region. In the presence of both compounds, the concentrations of the complexes of P with L and L–X are given by

$$[PL]=K[L]P_t/(1+K[L]+K_x[L-X]),$$
$$[P\cdot L-X]=K_x[L-X]P_t/(1+K[L]+K_x[L-X]),$$

where K_x is the constant for the association of P with L–X.

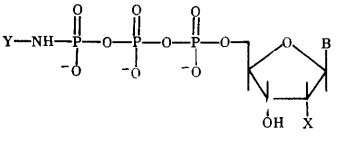
If a quantitative characteristic of a biological function F is proportional to the concentration of the complex, then, in the general case, where the complex P.L–X is also functionally active, we have

$$F=\alpha[PL]+\alpha_x[P\cdot L-X],$$

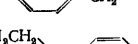
where α and α_x are proportionality coefficients. For an enzymic reaction, these characteristics are the rate constants for the conversion of the complexes PL and P.L–X into the enzyme–reaction product complex. If $\alpha_x = 0$, i.e. the complex with the reagent is functionally inactive, then L–X behaves as a competing inhibitor in relation to L.

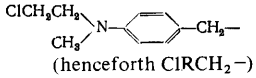
For the systems in which reactive derivatives of nucleic acids and their components have been investigated, several instances of the functional activity of affinity reagents are known.

Derivatives of nucleoside 5′-triphosphates, in the first place compounds (I, a–f), have found extensive applications in the study of nucleic acid polymerases:

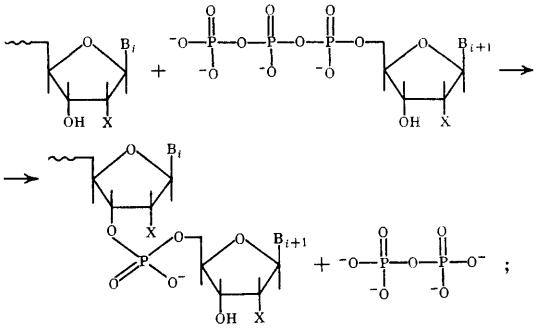


(Ia) B = adenine
(Ib) B = guanine
} X=OH, Y=

(Ic) B = thymine X=H, Y= 

(Id) B = adenine, X = H
(Ie) B = thymine, X = H
(If) B = adenine, X = OH
} Y = 
(henceforth ClRCH$_2$–)

Nucleic acid polymerases catalyse the synthesis of DNA molecules (DNA polymerases) or RNA (RNA polymerases) by transferring the nucleotide residue from nucleoside 5′-triphosphate to the growing polynucleotide chain:



X = H for DNA polymerases;
X = OH for RNA polymerases.

Henceforth in the review we shall employ widely the nomenclature adopted in the nucleic acid chemistry and approved by the International Union of Pure and Applied Chemistry (IUPAC) and the International Union of Biochemistry (IUB).[4] According to this nomenclature, the orthophosphoric acid residue is designated by p and the nucleoside residue by the initial letter of its name. The symbol p to the left of that of the nucleoside means that the phosphate is linked to the 5′-hydroxy-group, while p on the right means that the phosphate is linked to the 3′-hydroxy-group of ribose or deoxyribose. In the case of deoxyribonucleosides, the letter d is placed before the nucleoside symbol. In this formulation the reaction catalysed by polymerases is represented as follows:

$$\sim pN^i + pppN^{i+1} \xrightarrow[\text{(RNA polymerase)}]{} \sim pN^ipN^{i+1} + pp \quad ; \qquad (1)$$
$$\sim pdN^i + pppdN^{i+1} \xrightarrow[\text{(DNA polymerase)}]{} \sim pdN^ipdN^{i+1} + pp \; .$$

The most important feature of nucleic acid polymerases is their dependence on the template nucleic acid, RNA or DNA. Accordingly, one distinguishes RNA-dependent and DNA-dependent polymerases. The template nucleic acid promotes, at each stage of chain propagation, the selection of a fragment for incorporation in the growing chain of one of four monomers, complementary to the template nucleotide located in the decoding section of the enzyme. Since after the addition of a new monomeric fragment, the template shifts by one unit relative to the decoding section and the selection is carried out by the next template nucleotide, the nucleic acid is synthesised with the nucleotide sequence complementary to the template nucleic acid.

Studies carried out with three nucleic acid polymerases from *Escherichia coli* showed that the γ-amides of nucleoside triphosphates, in particular the reactive derivatives (Ia) and (Ib), are substrates of the DNA-dependent RNA polymerase.[5,6] On the other hand compounds (Ic) and (Id) are effective affinity reagents for a DNA-dependent DNA polymerase (DNA polymerase I)[7] and the RNA-dependent DNA polymerase.[8] The γ-amide of dTTP (Ic) was not found to possess substrate properties in relation to the DNA polymerase I. It has been

shown in relation to the γ-anilide of adenosine 5′-triphosphates† that not the pyrophosphate but the pyrophosphate anilide [*N*-phenylpyrophosphorimidate?] is liberated in the synthesis of RNA from this analogue.

The key enzymes in the biosynthesis of proteins are aminoacyl-tRNA-synthetases. Each of them catalyses the addition of a specific aminoacid to the corresponding transport RNA by forming an ester linkage between the aminoacid carboxyl and the OH group at the 3′-end of RNA. The process is coupled with the hydrolysis of ATP to adenosine 5′-monophosphate (AMP) and pyrophosphate:

$$R\overset{+}{C}H(NH_3^+)COO^- + pppA + tRNA - OH \rightleftarrows tRNA{-}OCOCH(NH_3^+)R + pA + pp \quad (2)$$

The reagent (Ia) is a competitive inhibitor for a broad spectrum of aminoacyl-tRNA-synthetases and cannot replace ATP as the substrate.[9–11] However, in the case of leucyl-tRNA-synthetases isolated from the chloroplasts and cytoplasm of *Euglena gracilis*,[12] compound (Ia) proved to be a substrate capable of replacing ATP in reaction (2).

The biosynthesis of protein takes place on ribosomes and is programmed by the template (information) RNA (mRNA). The aminoacid sequence in the protein synthesised is programmed in the mRNA by a sequence of trinucleotides (codons) which select from a mixture of aminoacyl-tRNAs one possessing an anticodon specifically recognised by the corresponding codon. The corresponding aminoacid is thereby selected. For example, polyuridylic acid $(pU)_n$ promotes the selection of phenylalanyl-tRNA with the anticodon –pGpApA–.

Analogously polyadenylic acid $(pA)_n$ promotes the selection of the ribosomal lysyl-tRNA. The selected aminoacyl-tRNA reacts with the growing polypeptide chain, present on the ribosome in the form of peptidyl-tRNA, in the following manner:

$$\begin{aligned} &NH_3^+CH(R^1)CO - NHCH(R^2)CO - \ldots NHCH(R^i)CO - tRNA^i + \\ &+ NH_3^+CH(R^{i+1})CO - tRNA^{i+1} \rightarrow NH_3^+CH(R^1)CO - \ldots \\ &- NHCH(R^i)CO - NHCH(R^{i+1})CO - tRNA^{i+1} + tRNA^i. \end{aligned} \quad (3)$$

In the presence of polyuridylic acid and even of its short fragments down to $(pU)_3$, phenylalanyl-tRNA is therefore bound to the ribosome. In the presence of polyadenylic acid, Lys-tRNA is bound to the ribosome. It has been found that the alkylating derivatives of oligonucleotides $(pN)_n$, carrying the *N*-2-chloroethyl-*N*-methylaminophenyl fragment ClR either at the 5′- or the 3′-end also stimulate the binding to the ribosome of the aminoacyl-tRNA coded by them, i.e. the introduction of a reactive group in the 3′- or 5′-position does not disturb the functional activity of the oligonucleotide.[13–15]

Thus the affinity reagents L–X either function together with the ligand L or behave as competitive inhibitors of the function performed by the biopolymer. Naturally, reversible inhibition must be studied under conditions where the chemical activity of L–X, resulting in the covalent binding of L–X to the recognition region of the biopolymer, is not manifested. This can be readily achieved in the case of photoactive reagents, for example the reagents (Ia) and (Ib), which react under ultraviolet irradiation, which converts the azide, chemically inert under physiological conditions, into the highly reactive nitrene biradical. For this, it is sufficient to investigate the functional activity of P in the presence of L and L–X in the dark. Otherwise, it is necessary to employ fairly rapid tests for functional activity carried out over a period significantly shorter than the time of the chemical reaction of L–X in the complex with P. For certain reagents it is possible to convert the reactive derivative into an inactive derivative with a very similar structure. For example, having kept the reagents (Id) and (If) in water for a time sufficient to hydrolyse the C–Cl bond, it is possible to obtain from $ClRCH_2NHpppN$ the derivative $HORCH_2NHpppN$ similar in structure and hence in affinity to the biopolymer, to investigate its inhibiting activity as a function of the polymer being studied, and hence to estimate its affinity for the biopolymer.

The rate of the affinity modification is

$$v = k[P{\cdot}L - X] = \frac{kK_x[L - X]P_t}{1 + K[L] + K_x[L - X]},$$

where k is the rate constant for the reaction of L–X with P in the complex P.L–X.

When the affinity reagent (and the natural ligand when the latter has been introduced into the reaction mixture) are present in a sufficient excess relative to the polymer and do not undergo side reactions, we have

$$v = \frac{kK_x[L - X]_0 P_t}{1 + k[L]_0 + K_x[L - X]_0},$$

where $[L]_0$ and $[L–X]_0$ are the initial concentrations. Since the total concentration of the biopolymer decreases in affinity modification, we have

$$P_t = (P_t)_0 - [L - X - P],$$

where $(P_t)_0$ is the initial concentration of the biopolymer and L–X–P is the product of the affinity modification. In this case the process is a pseudofirst-order reaction:

$$v = \frac{d[L - X - P]}{dt} = \frac{kK_x[L - X]_0}{1 + K[L]_0 + K_x[L - X]_0}\{(P_t)_0 - [L - X - P]\}.$$

It follows from this expression that the dependence of the apparent rate constant on the concentration of the affinity reagent is hyperbolic and the natural ligand inhibits the affinity modification process (it is usually said that it protects the polymer against affinity modification). Both these findings are important criteria, whose fulfillment shows that the process investigated proceeds via the affinity modification mechanism.

If the addressed section of the reagent is fixed in the recognition region as a result of the affinity modification, the interaction of the natural ligand L with the biopolymer P is significantly hindered or becomes altogether impossible, i.e. the biopolymer becomes functionally inactive. Assuming that the functional activity of the biopolymer, retained at a specific instant, is proportional to the concentration of the unmodified biopolymer, it is possible to follow the course of the affinity modification from the inactivation of the biopolymer, which is described by a kinetic equation for a pseudo-first-order reaction in the presence of a sufficient excess of L–X in relation to the polymer:

$$-\frac{dF}{dt} = k_{app}F = \{kK_x[L - X]_0/(1 + K_x[L - X]_0\}F.$$

All the equations presented were derived on the assumption that L–X is consumed only in the reaction with the polymer in the complex P.L–X. If the reagent has been taken in excess relative to P, the reaction proceeds until the polymer has been completely consumed. However, in fact, sufficiently active groups X can as a rule react also with water, with the buffer components of the medium, and also with the biopolymer itself without preliminary complex formation, including its sections which have no direct bearing on the recognition region. The group X then reacts and loses its reactivity, while the address remains unaltered, i.e. the affinity for the

†Adenosine 5′-triphosphate (ATP) is the substrate or effector in hundreds of different enzymic reactions and its reactive derivatives and analogues are widely used in the study of the corresponding enzymes.

biopolymer is retained. The reaction product L–R becomes an inhibitor of the affinity modification with a constant K_r, which is the constant for the association of L–R with P. A kinetic analysis of this process has been carried out[16] on the assumption that the reagent has been taken in significant excess. The equation of the kinetic curve in the general case where $K_r = K_x$ is

$$[L-X-P]/(P_t)_0 = 1 - \left[\frac{1+K_x[L-X]_0}{1+K_r[L-X]_0-(K_r-K_x)[L-X]_0\exp(-k_0 t)}\right]^{\frac{\gamma K_x}{K_r-K_x}}.$$

In this case the reaction does not go to completion, i.e. the degree of conversion of P into L–X–P does not reach unity even in the limit:

$$\{[L-X-P]/(P_t)_0\}_{t=\infty} = 1 - \left(\frac{1+K_x[L-X]_0}{1+K_r[L-X]_0}\right)^{\frac{\gamma K_x}{K_r-K_x}}, \quad (4)$$

where k_0 is the pseudofirst-order rate constant for the reaction of L–X in solution with water and other components and $k_0\gamma$ is the rate constant for the conversion of the complex P.L–X into the affinity modification product. The degree of conversion at the end of the reaction can be measured with a sufficient accuracy even when the affinity modification is rapid and it is difficult to obtain the kinetic characteristics of the process. Evidently, in a suitable range of concentrations, it is possible to obtain from Eqn.(4) the association constants K_x and K_r as well as the quantity γ, which are present in Eqn.(4) as independent parameters.

The kinetics of the affinity modification become complicated still further when the interaction of P with L–X is a complex reaction proceeding via the formation of active intermediate species. This process has been considered by Knorre and co-workers,[17,18] such consideration being outside the framework of this review.

III. THE PRINCIPAL PROBLEMS SOLVED BY THE METHOD OF AFFINITY MODIFICATION AND THE GENERAL PRINCIPLES OF THE CONSTRUCTION AND USE OF AFFINITY REAGENTS

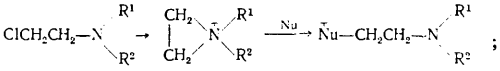
The nature of the reactive group of the affinity reagent, the method of introducing it into a natural ligand or its analogue, the carrier of affinity for the biopolymer (address), and the method used to carry out the affinity modification are to a large extent determined by the problem which has to be solved with the aid of the given reagent. Therefore, before proceeding to a systematic description of the different types of reactive derivatives of nucleic acids and their components, we shall consider the principal problems in the solution of which the method of affinity modification is used and the requirements arising from this which must be met by the affinity reagents and by the procedures employed for the affinity modification.

We shall begin with the question of the investigation of the region of the specific interaction of the biopolymer with the ligand with the aid of a reactive derivative of the ligand.

In its most simplified form, this approach presupposes that the addressing component of the reactant is fairly rigidly fixed in the recognition region via non-covalent interactions, after which the biopolymer is attacked by the reacting group and the reagent is covalently fixed in the same region. For a biopolymer with a known primary structure, it is then determined which particular aminoacid or nucleotide residue has been chemically modified. The monomeric fragment located in the recognition region or in its immediate vicinity is thereby found. If the three-dimensional structure of the biopolymer is known and data or fairly reliable ideas about the conformation of the reagent are available, it is possible to determine the entire region in which the biopolymer interacts with the address.

Clearly the rigid fixation of the address should sharply limit the region of contact between the biopolymer and the reacting group and hence the region in which chemical modification can occur. For it to actually occur, it is necessary that in this region there should be at least one group capable, in principle, of chemical interaction with the reagent employed. This is more probable the less selective the reacting group.

From this point of view, among heterolytic processes the most favourable are the reactions of strong and only weakly selective electrophiles with numerous nucleophilic centres of proteins and nucleic acids. The latter include the imidazole rings of the histidine residues, the ε-amino-groups of the lysine residues, the carboxy-groups of the aspartate and glutamate residues, the hydroxy-groups of the serine, threonine, and tyrosine residues, the SH groups of the cysteine residues, the carbonyl oxygen of the peptide bonds and glutamine and asparagine residues, the terminal amino- and carboxy-groups of the polypeptide chains, many positions in the heterocyclic bases of nucleic acids, and the phosphodiester internucleotide and terminal phosphomonoester groups of the polynucleotide chains. Among the reacting groups of this type in affinity reagents based on nucleic acids and their components, the moderately reactive CH_2ICO and CH_2BrCO groups and the aromatic and aliphatic 2-chloroethylamino-groups have found the greatest applications at the present time. The former react via a direct mechanism and the latter via the intermediate formation of highly electrophilic ethyleneimmonium cations:

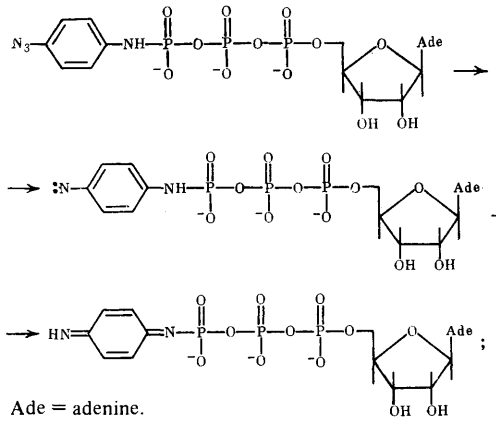


Nu = nucleophile.

For aromatic 2-chloroethylamines, the first stage is rate-limiting[19] and the intermediate cations are extremely reactive and do not accumulate in measurable concentrations, reacting almost instantaneously with nucleophiles, including water, which is invariably present when biopolymers undergo affinity modification. Their reactivity in relation to nucleophiles has come to be characterised by the competition factor, which is defined as the ratio of the rate of reaction with the nucleophile to the rate of reaction with water divided by the concentration of the nucleophile.[20]

Pt^{2+} derivatives have also been proposed recently as the reacting groups in affinity reagents for attack on nucleophilic centres.[21,22]

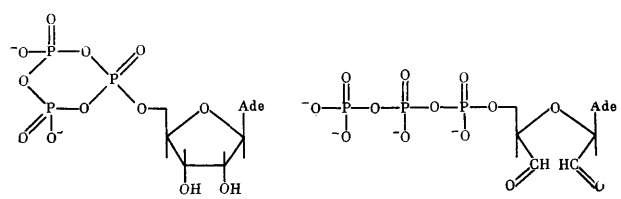
According to data obtained in anhydrous model systems, the singlet nitrene R–N:, capable of being inserted in X–H bonds, including C–H bonds, is even less selective. Derivatives of aryl azides, which generate nitrenes on irradiation with ultraviolet light, have therefore found extensive applications as affinity reagents. The potentially singlet nitrene can modify even the side groups in hydrophobic aminoacids–alanine, valine, leucine, isoleucine, phenylalanine, and proline. However, recent investigations of the behaviour of nitrenes in aqueous solution have shown that rapid secondary reactions, which depend significantly on the nature of other groups in the same benzene ring, are characteristic of these species.[23–24] Thus it has been established that compound (Ia) namely the γ-p-azidoanilide of ATP, is rapidly converted into a quinone imine imide on irradiation of its aqueous solution with ultraviolet light.[25]



Ade = adenine.

This compound is a powerful electrophile which reacts with imidazole, morpholine, and mercaptoethanol, but its selectivity is significantly higher than that of nitrenes.

For reagent (Ia) as an example, it is seen that, apart from the address, which in the given instance is the ATP residue, and the reacting group, it contains the connecting phenylamide fragment (spacer). For a rigid fixation of the address, the modification takes place in this instance outside the recognition region. Such reagents have come to be called exoreagents. For the reacting group to come into contact with the active centre, it is desirable that it be part of the composition of the address itself, i.e. that an endoreagent be employed. Naturally, this can be done only at the expense of some distortion of part of the address, having made sure that such distortion does not alter sharply the affinity for the biopolymer. Adenosine 5'-trimetaphosphate (II) (ATMP) or the product of the oxidation of ATP with periodatate at the *cis*-diol group (oATP) may serve as examples of endoreagents.



ATMP oATP

The former is a powerful phosphorylating reagent and, as a result of the modification, the ATP residue is directly bound to the nucleophilic centre of the biopolymer. The latter is capable of forming Schiff bases with the ε-amino-groups of lysine residues via the aldehyde groups.

A number of attempts at direct photochemical cross-linking of nucleic acids and their components in complexes with biopolymers have been described. By virtue of the short life of the excited state, one may expect that modification takes place directly in the region of the interaction of the chromophore with the biopolymer. However, the nature of the products formed and their stability, including their stability under conditions necessary for the subsequent identification and localisation of the modified fragment, have so far been little investigated and it is as yet impossible to assess the likely usefulness of this approach for the determination of the recognition region.

As already mentioned, the idea of the rigid fixation of the address is not itself non-controversial. Any recognition is ensured by a multipoint interaction. Less populated states with interaction via an incomplete set of points should therefore exist in the biopolymer–ligand complex together with the state in which all the contact points are employed. As a result of this, the reacting group can acquire a significant mobility. Biopolymers are also not rigid molecules and comprise different conformations in different proportions, as shown by the ability of many biopolymers to undergo specific conformational transitions. The biopolymer–ligand complex can therefore be represented by a multiplicity of states with different mutual orientations of the reacting group and the reactive sections of the biopolymer. The probability of affinity modification is determined not only by the population of a particular state but also by the extent to which this state is favourable for chemical reaction. Therefore, as a result of the modification of the biopolymer by the affinity reagent, the address may be fixed in a state which differs significantly from the functionally significant state and can actually be displaced from the recognition region, as shown schematically in Fig. 1.

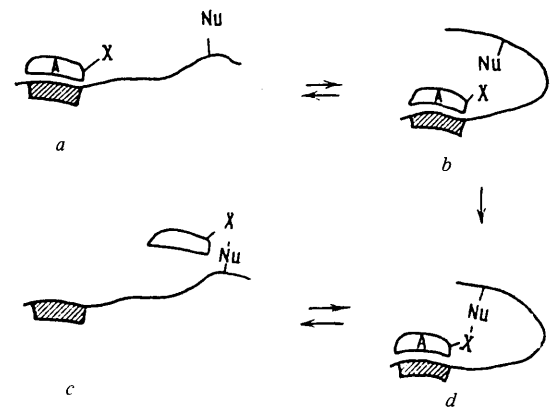


Figure 1. Schematic representation of the modification of a biopolymer at the nucleophilic centre by means of an Nu reagent consisting of the address A and the electrophile X, which leads to the fixation of the address outside the recognition region (shaded part): *a*) predominant conformation of the biopolymer–reagent complex; *b*) conformation present in a small proportion but having a favourable mutual disposition of the reacting groups; *c*) the same conformation after the reaction; *d*) predominant conformation of the modification product.

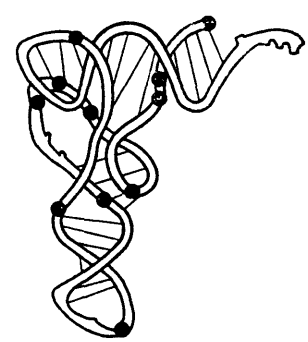


Figure 2. The positions in the structure of phenylalanine tRNA from *E. coli* of the guanosine residues (filled circles) through which groups capable of photoactivation are introduced statistically in the preparation of the azido-tRNA affinity reagent.[37]

It follows from all the foregoing features that even small changes both in the recognition region of the biopolymer and in its immediate environment as well as in the structure of the reagent can exert a drastic influence on the process and the result of the affinity modification. We shall present several examples.

As already stated, compound (Ia) is a competitive inhibitor of aminoacyl-tRNA synthetase from *E.coli*[9] and tryptophanyl-t-RNA synthetase from the ox pancreas.[10] In both cases ultraviolet irradiation of the complex of compound (Ia) with the enzyme entails the covalent addition of the reagent to the enzyme. However, whereas in the latter case it is accompanied by the inactivation of the enzyme, the addition of up to 20 residues of the reagent to phenylalanyl-tRNA synthetase does not lead to the loss of kinetic activity, i.e. the address remains fixed outside the ATP recognition region. The replacement of the *p*-azidoaniline residue in compound (Ia) by the *p*-azido-*N*-methylbenzylamine residue gives rise to a reagent which adds photochemically to phenylalanyl-tRNA synthetase and inactivates the enzyme.[26]

On irradiation with ultraviolet light, the reagents (Ie) and (Id) inactivate the RNA-dependent DNA polymerase and DNA polymerase(I) from *E.coli*. However, in order to obtain the same level of inactivation of the enzyme a concentration of the reagent lower by a factor of 50 is required in the first case compared with the second case.

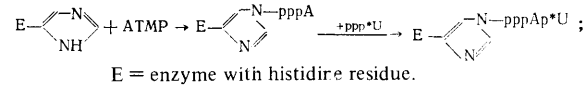
The reagent (If) has been investigated as an affinity reagent in relation to yeast hexokinase—the key enzyme in carbohydrate metabolism, catalysing the transfer of the orthophosphate residue from ATP to the 6-hydroxy-group of glucose. Depending on the pH of the medium, the enzyme exists in the monomeric or dimeric form. It has been found that compound (If) is not a competitive inhibitor of the monomeric hexokinase and accordingly does not inactivate the active centre of the enzyme. On the other hand, it has an affinity for the dimeric form of hexokinase comparable to that of ATP and inhibits this enzyme irreversibly.[27] It is of interest to note that an analogous derivative of AMP, namely $ClRCH_2NHpA$, inhibits irreversibly the monomeric form of hexokinase via the affinity modification mechanism, but does not act on its dimeric form.[28]

Thus the same reagent can behave very differently in relation to biopolymers fulfilling isotypical functions or in relation to different states of the same biopolymer. On the other hand, the examples presented have shown that, by introducing certain changes into the structure of the address of the spacer fragments, it is usually possible to find a suitable affinity reagent for the biopolymer investigated.

Together with a change in the structure, it is possible to influence the results of the affinity modification by altering the method by which it is carried out. A procedure has been proposed[29] which can find fairly wide-scale applications in the affinity modification of enzymes catalysing two- and three-substrate reactions. The initial stage of the reaction catalysed by the RNA polymerase from *E.coli* has been investigated and it was found that in the presence of the substrates pppA and pppU in conjunction with the template employed (a fragment of the T7 bacteriophage DNA) the enzyme catalysed the reaction

$$pppA + pppU \rightarrow pppApU + pp\ .$$

The use of ATMP as the affinity reagent can lead to its non-specific modification by virtue of its high reactivity. However, when ATMP was added to the enzyme, the subsequent addition of the second unit of the polynucleotide chain is possible only when the PPPA fragment is bound in the region of the active centre of the enzyme. When non-radioactive ATMP and UTP labelled with ^{32}P in the α-position in the triphosphate fragment are used, the radioactive label is found only in the section corresponding to the active centre of the enzyme. It has been shown that the addition is to a histidine residue:[29]



E = enzyme with histidine residue.

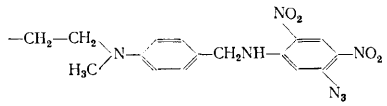
All that has been said above demonstrates that the synthesis and application of affinity reagents, suitable for the location of individual sections of monomers in the recognition region, is by no means the trivial task it might have appeared to be on the basis of a simplified model of affinity modification. It is therefore not surprising that only a limited number of reliably interpreted results have so far been obtained on these lines.

The problem of elucidating the functional significance of individual subunits in multisubunit structures with the aid of affinity modification appears much simpler. In this case it is sufficient that the reaction should have occurred within the limit of the subunit which interacts with the address. The greatest number of studies of this kind have been carried out with ribosomes and in particular with the ribosomes from *E.coli*, for which the primary structure of all the RNA molecules constituting the ribosome (ribosomal RNA or rRNA) and all the 53 proteins are now known. The identification of the regions corresponding to the binding of mRNA, namely two tRNA molecules carrying the peptide and aminoacyl residues (the P and A sites in ribosomes), as well as the region catalysing the transfer of the peptide residue to the aminoacyl-tRNA, the so-called peptidyltransferase centre, is of primary interest. Since the region where the codon–anticodon interaction takes place is of greatest importance for the mRNA recognition region, reactive derivatives of oligonucleotides containing one or several codons are widely used. Since the modifying proteins and rRNA fragments are identified by electrophoresis on the basis of the determination of electrophoretic mobilities, it is important that the large oligonucleotide or polynucleotide should be removed before identifying the modified component. For this purpose, it is convenient to employ reagents from which the address can be split off under fairly mild conditions. The oligoribonucleotide derivatives $ClRCH_2NH(pN)_n$ and $(pN)_n > CHRCl$, mentioned in the previous Section, in which the alkylating fragment is joined to the address via either a phosphoramide or an acetal linkage, satisfy this condition particularly well. Both types of linkage are fairly stable under the conditions of affinity modification but readily hydrolyse in a weakly acid medium.

In many cases the region of the interaction of the polymeric address with a complex subunit structure is fairly extensive. In particular, the regions of the interaction of mRNA and tRNA with a ribosome embrace a number of components of the ribosome, both rRNA and proteins. In order to identify this region by the traditional procedure based on the use of an individual compound as the affinity reagent, it is necessary to have a set of reagents with different positions of the reacting group relative to the address. Thus, in a study of the region in which mRNA is bound to ribosomes from *E.coli* and from rat liver[14,30–32] with the aid of alkylating derivatives of oligouridylates, it was found that both the distribution of the label between rRNA and the proteins and the sets of the modified proteins differ sharply depending on the end (3′ or 5′) of the oligonucleotide address to which the *N*-2-chloroethyl-*N*-methylaminophenyl fragment is linked.

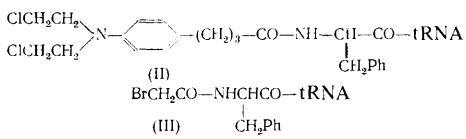
The synthesis of a large set of derivatives with different fixed positions of the reactive groups is fairly laborious for a polymeric address, for example, tRNA. It is therefore convenient to use as reagents for the first stage of the investigation derivatives in which the active groups are scattered statistically throughout the polymer molecule. The number

of such groups in each individual tRNA molecule should be small, not more than 2–3, in order not to disturb the ability of tRNA to interact specificially with the ribosome. tRNA derivatives containing fragments capable of being photoactivated have been synthesised for this purpose:



They are bound covalently to numerous tRNA guanine residues (Fig.2).[33] When 1–2 such residues are present on the molecules of the phenylalanine tRNA from *E.coli*, the latter retain the ability to bind phenylalanine enzymically and the resulting phenylalanyl-tRNA is bound selectively to the ribosome in the presence of poly-U. There derivatives (azido-tRNA) have found extensive applications in the study of the regions in which tRNA is bound to the ribosome in various functional states of the latter.[34,35]

The problem of the region corresponding to the interaction of phenylalanine tRNA with phenylalanyl-tRNA synthetase from *E.coli* has also been solved with the aid of azido-tRNA.[33] The above enzyme consists of two types of subunits—α and β. The problem was initially investigated with the aid of alkylating derivatives of tRNA carrying reactive groups on the aminoacyl fragment:



At first sight contradictory results were obtained: the first reagent alkylated predominantly the α-subunit[36] while the second alkylated mainly the β-subunit.[37] The use of azido-tRNA showed that, when the complex of the enzyme with the above derivatives is irradiated, tRNA adds predominantly to the β-subunit.[33] The fact that, for a substituent of small size at the α-amino group, the β-subunit is also alkylated and that after an increase in the size of the substituent mainly the α-subunit is alkylated permitted the additional conclusion that the acceptor end of tRNA in the complex with the enzyme is located near the region where the subunits come into contact.

Yet another problem in the solution of which affinity reagents can find extensive applications is that of the determination of the primary structure of large polymer molecules, for example, DNA. An important stage in the determination of the primary structure is the selective cleavage of the large polymer molecule into fragments of moderate length. In relation to DNA, this problem is solved with the aid of special restriction enzymes, which selectively cleave DNA in the vicinity of specific nucleotide sequences. At the same time, there are many chemical methods for the cleavage of DNA. For example, alkylation of the purine bases leads to their elimination, which makes it possible to cleave DNA under alkaline conditions in the depurinated sections. DNA is also cleaved in the presence of Fe^{2+} ions and O_2. For this purpose Fe^{2+} should be chelated, which is achieved either with the aid of special antibiotics, for example, bleomycin, or with the aid of model chelating agents, such as ethylenediaminetetra-acetic acid.[38] The cleavage of DNA with the aid of dyes on irradiation by a 337 nm laser having a high irradiation density has been described recently.[39] The cleavage takes place as a result of the absorption by the dye of two quanta and the subsequent radiationless excitation energy transfer to the σ-bonds of the ribose phosphate skeleton.

The addition of the corresponding reactive groups to oligonucleotides of specific structure leads to the prospect for the selective cleavage of DNA and RNA in the vicinity of sections complementary to the addressing oligonucleotides. Fig.3 presents the results obtained when a DNA fragment is treated by an addressed alkylating reagent complementary to the single-stranded section of this fragment.[40]

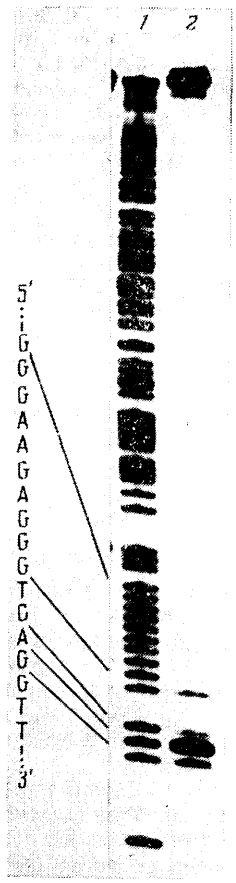


Figure 3. Results of the electrophoretic analysis in a polyacrylamide gel (autoradiograph) of the products of the cleavage of the 303-nucleotide single-stranded DNA fragment labelled at the 3'-end with the ^{32}P radioisotope after the complementarily addressed alkylation with the reagent $ClRCH_2$. .NHd(pTpGpApCpCpCpTpCpTpTpCpCpCpA) which is complemetary to the sequence of the fragment TpGpGpGpApApGp. ApGpGpGpTpCpA and after treatment with piperidine in order to achieve cleavage at the alkylated purines: *1*) products of the partial degradation of the fragment at the purine nucleotides (marker for the determination of the cleavage sites); *2*) products of the degradation of the fragment obtained with the aid of the complementarily addressed modification.[40]

In all the cases described above we were dealing with the use of affinity reagents as research instruments. However, another application of these reagents has begun to develop vigorously, namely the application involving specific action on biological processes. We shall consider this aspect in

relation to the approaches whereby nucleic acids, i.e. the genetic apparatus, can be specifically acted upon.

It is known that chemical influences on nucleic acids have found extensive applications for the preparation of modified forms of living organisms resulting from a change in the DNA structure (mutations). Such influences on nucleic acids are used in oncology for the suppression of the multiplication of malignant tumour cells, in certain special situations for the suppression of the immune response by the organism, for example, for the prevention of the rejection of surgically transplanted kidneys, and to regulate the multiplication of viruses in viral infections. In all the cases described one is dealing with relatively unselective reagents, which make an impact on all nucleic acids. Thus, in chemical mutagenesis the changes occur statistically in all the genes, generating numerous, as a rule unfavourable or even lethal, changes in the genetic apparatus. However, when one is dealing with micro-organisms or plants, the few mutations which impart to the organism a feature which is of interest from the practical point of view can be discovered by subsequent selection. Such selection can lead to the creation of new forms of plants and micro-organisms. When chemical reagents acting on nucleic acids, namely derivatives of 2-chloroethylamine, *cis*-dichlorodiammineplatinum, and others are used, in some cases it is possible to select doses which effectively arrest the growth of the tumour but are not yet lethal for the human organism as a whole. In those few cases where this can be achieved, chemotherapy makes it possible to prolong life and sometimes also to effect a radical cure of the patient.

The prospect of increasing the selectivity of such reagents and in the ideal case of creating reagents which would suppress the multiplication of viruses or cancer cells without harming healthy cells and would also suppress the multiplication of the immunocompetent cells (T-lymphocytes) which are designed to reject transplanted organs but would not act on cells fulfilling other numerous protective functions in the living organism is attractive. One of the imaginable pathways leading to the fulfillment of this aim involves the creation of complementarily addressed reagents on the basis of oligonucleotides or nucleic acids complementary to the affected target. This problem was formulated in a general form for the first time by Summerton.[41]

In order to realise fully this prospect, it is necessary to solve a number of new problems. In the first place, we are dealing with the creation of reagents acting on nucleic acids but at the same time possessing components having the same chemical composition and acting as the address. It is necessary to prevent to the maximum possible extent the action of the reacting group on the address itself, particularly in the numerous preliminary operations. One of the possible procedures involves the application of reacting groups whose reactivity is regulated in some way. It has been suggested[42] that the *N*-2-chloroethylalkylaminophenyl group, having the formyl residue in the *para*-position in the benzene ring, be used for this purpose. As a result of the strong electron-accepting effect of the formyl group, the alkylating properties of the 2-chloroethylamino-group are weak. This makes it possible to obtain nucleic acid derivatives of interest to the experimenter virtually without any risk of alkylating the address. Directly before using the reagent, it is possible to reduce the formyl group to the hydroxymethyl group, which increases by two orders of magnitude the reactivity of the *p*-*N*-2-chloroethyl-*N*-methylaminophenyl residue.

If we think of the future employment of complementarily addressed reagents as medical preparations or for the induction of mutations in living organisms but not in isolated DNA molecules, it is necessary to take into account, in the synthesis of the reagents, the possibility of the degradation of the address by nucleases and the necessity for the reagent to cross the outer and inner membranes of the target cells.

Studies on affinity modification involving living objects are in the very initial stage. In relation to the alkylation of derivatives of oligothymidylates with one uridine residue at the 3′-end, carrying at this end the alkylating groups $(dTp)_nUCHRCl$, it has been shown that they modify the complementary polyadenyl fragments in the cells of the Krebs ascites carcinoma, such fragments being usually located at the 3′-end of the mRNA of higher organisms.[43] At the same time it has been shown that the address is preserved and the high selectivity of the alkylation reaction has been demonstrated: the degree of modification of the fragments of poly-A exceeded by two orders of magnitude the degree of modification of the remaining nucleic acids in the cells. In order to increase their ability to permeate through the membrane, oligonucleotides with ethylated internucleotide phosphates $[dTp(C_2H_5)]_nUCHRCl$ were used.[44] The penetration into the cell was then significantly greater than in the case of the non-ethylated negatively charged address. The first successful data concerning the possibility of the effective modification of viral nucleic acids in cells and specific mRNA of the cells were obtained in experiments designed to suppress the development of the influenza virus in the cells of chicken fibroblasts[45] and to suppress the synthesis of immunoglobulins in the tumour cells of mouse myeloma.[46]

IV. REACTIVE DERIVATIVES OF NUCLEOSIDES AND NUCLEOSIDE MONO-, DI-, AND TRI-PHOSPHATES

Nucleosides and nucleoside mono, di-, and tri-phosphates are the simplest compounds containing chemical structures characteristic of nucleic acids: the heterocyclic bases, ribose or deoxyribose, and phosphoric acid residues. In order to obtain affinity reagents, it is possible to introduce reactive groups into each of these structures.

Reactive groups are frequently introduced into heterocyclic bases by their halogenation and subsequent substitution of the halogenated compounds. The widely employed derivatives of purine nucleoside polyphosphates having the azido-group in the 8-position as well as derivatives of purine nucleoside polyphosphates having SH or azido-groups in the 6-position may serve as examples of derivatives obtained in this way.

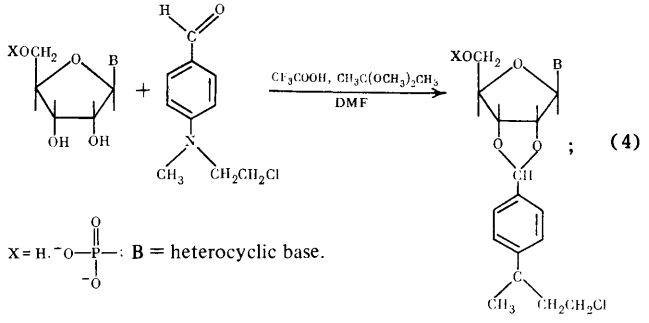
Such derivatives are affinity reagents of the endo-type, since the most specific fragments of the structure of nucleoside polyphosphates, recognised by enzymes, are their heterocyclic bases. A second approach to the introduction of reactive groups into heterocyclic bases leads to the formation of reagents of the exo-type and is based on the application of heterobifunctional reagents containing two groups with different chemical properties. One of the groups of the reagent ensures its addition to the heterocyclic base, while the other correspondingly becomes the reactive group of the affinity reagent obtained. Thus photoactivatable and arylating affinity reagents have been obtained by acylating the amino-groups of purine nucleoside polyphosphates by the halide of the corresponding substituted carboxylic acids.[47]

In the studies of the properties of derivatives of nucleoside polyphosphates having reactive groups in the heterocyclic bases it was observed that as a rule they differ sharply from the normal substrate in terms of their ability to interact with enzymes. For example, the analogue of guanosine triphosphate with the 4-azidobenzyl residue in the amino-group could not be used for the affinity modification of the enzyme adenylate cyclase, since its affinity for this enzyme was too low.[47] This is not surprising, because it is known that heterocyclic

bases play the main role in ensuring the specificity of such interactions. The introduction of substituents into heterocyclic bases should influence their interaction with enzymes and can influence their conformational state. Thus the 8-azido-derivatives of purine nucleoside polyphosphates mentioned above have the *anti*- and not the *syn*-conformation, in contrast to the normal substrates.[48] The synthesis and properties of derivatives of nucleoside polyphosphates having reactive groups in the heterocyclic bases have been recently considered in a number of reviews[48–50] and will not be discussed here.

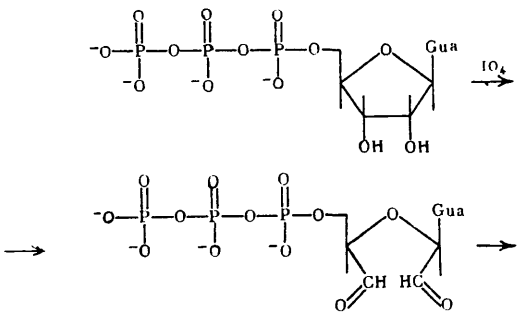
The principal method for the modification of ribose and deoxyribose involves the acylation of their hydroxy-groups. A number of derivatives with sulphonylating and aryl azide groups in the 2′(3′)-positions in ribose have been obtained by acylating adenosine polyphosphates.[49] Acylation of adenosine and subsequent separation of the product yielded derivatives with alkylating or sulphonylating groups in the 5′- or 2′(3′)-positions in ribose.[51,52]

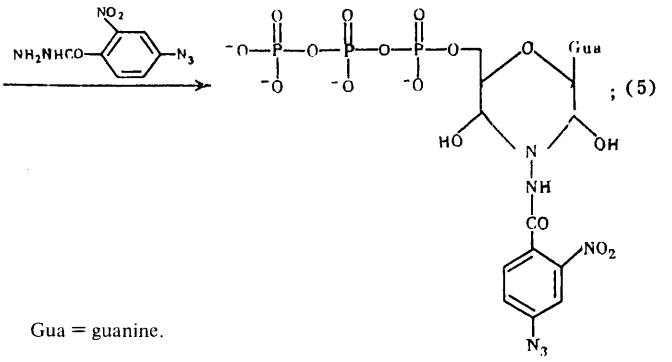
A method has been developed for the introduction of the alkylating fragment at the 2′,3′-cis-diol group. For this purpose, the nucleoside or nucleotide is treated in anhydrous dimethylformamide with 4-(*N*-2-chloroethyl-*N*-methylamino)-benzaldehyde in the presence of CF_3COOH and dimethoxypropane. Derivatives of uridine, adenosine, cytidine, and all four 5′-nucleotides have been obtained in this way.[53–56]



However, they have been tested as affinity reagents only at the level of oligo- and poly-nucleotides and will be discussed in the next Section.

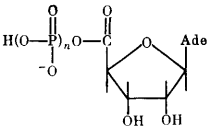
The oxidation of nucleosides and their polyphosphates by periodate leads to the cleavage of the furanose ring at the 2′,3′-diol group with formation of a reactive centre—the dialdehyde group. The latter can itself interact reversibly with the amino-groups of proteins via the formation of Schiff bases. The reduction of Schiff bases with tetrahydroborates leads to the irreversible binding of the reagents to the amino-derivatives. The nucleoside polyphosphates oxidised at the ribose residue have been used for the affinity modification of many enzymes.[49] The reaction of the ribose-oxidised guanosine triphosphate with a bifunctional hydrazide reagent yielded a derivative with an aryl azide group:[57]





Gua = guanine.

Derivatives of adenosine mono- and tri-phosphates, capable of reacting with the nucleophilic groups of proteins, have been obtained by phosphorylating adenosine oxidised at the 5′-carbon atom:[58,59]



$n = 1, 3$.

Reactive groups can be introduced into the structure of nucleoside polyphosphates by replacing the entire phosphate group or part of it. Many reagents of this type have been described in reviews[48–50] and many of them have been used as affinity reagents. However, numerous facts indicate that this method of introducing reactive groups into the structure of nucleoside polyphosphates is non-optimum, since the decrease of the overall negative charge of the molecule has a significant influence on its interaction with enzymes. Evidently the most rational procedure for the synthesis of affinity reagents derived from nucleoside polyphosphates involves the introduction of the reactive groups into their terminal phosphates. Derivatives of nucleoside triphosphates, which are the substrates of hundreds of enzymic reactions and which have reactive groups at the γ-phosphate residue, are of greatest interest. It is to be expected that the ability of the molecule as a whole to undergo specific interactions is least disturbed in such derivatives, because neither the base nor the carbohydrate component of the molecule have been affected and only the charge of the triphosphate group has been reduced by unity.[60] The vast majority of enzymic reactions with participation of nucleoside triphosphates represent either phosphate transfer or the transfer of the nucleotide residue to an acceptor, so that the triphosphate group should be located directly in the active centre of the enzyme near the acceptor binding centre. For this reason, reactive γ-derivatives of nucleoside triphosphates can be used also for the investigation of the acceptor binding sections.

In order to obtain derivatives of nucleoside 5′-triphosphates containing different substituents bound to the γ-phosphate, a simple general method, based on their conversion, with the aid of carbodiimides, into nucleoside 5′-trimetaphosphates, has been developed. The reaction can proceed both in an anhydrous medium using dicyclohexylcarbodiimide and in an aqueous solution using a water-soluble carbodiimide. The resulting nucleoside 5′-trimetaphosphate readily reacts with amines to form the corresponding γ-amides. Examples of compounds obtained in this way are compounds (I, a–f).[61–63]

In conformity with general considerations, it has been found that such γ-amides exhibit an affinity for the majority of the enzymes investigated in the class of hydrolases,

phosphotransferases, and synthetases and, as already mentioned, in some cases can serve as the substrates of these enzymes (see Section II). A systematic account of the data published up to 1980 has been given in the review of Grachev et al.[64] Since that time, the range of enzymes and protein factors investigated has expanded.

It has been shown that the derivative (If) is an affinity reagent in relation to the enzyme catalysing the reversible phosphorolysis of the terminal group in pCpCpA, which is a property characteristic of all transport RNA (ATP, CTP: tRNA nucleotidyl transferase):[65]

$$\text{tRNA-pXpCpCpA + pyrophosphate (pp)} \rightleftarrows \text{tRNA-pXpCpC + pppA,} \quad (5)$$

$$\begin{aligned}&\text{tRNA-pXpCpC + pp} \rightleftarrows \text{tRNA-pXpC + pppC,}\\ &\text{tRNA-pXpC + pp} \rightleftarrows \text{tRNA-pX + pppC;}\\ &\text{X = A, C, G, or T.}\end{aligned} \quad (6)$$

It is also an affinity reagent in relation to acetylcoenzyme A carboxylase, catalysing the conversion of acetyl-CoA into malonyl-CoA:[66]

$$\text{ATP} + HCO_3^- + CH_3CO\text{-CoA} \rightarrow \text{ADP} + p + {}^-OOC-CH_2-CO\text{-CoA},$$

and being of key importance for the biosynthesis of aliphatic acids and in relation to the Na^+, K^+-dependent ATPase, which plays the main role in the transmembrane transport of sodium and potassium ions.[67] It has been established that compound (Ib), a photoactive derivative of GTP, effects the affinity modification of the GTP-dependent protein initiation factor involved in the initial stage of the biosynthesis of proteins in eukaryotic organisms. Among the three subunits of the factor, the γ-subunit is modified exclusively.[68] It has been demonstrated in relation to creatine kinase, an important enzyme in bioenergetic processes in mice, catalysing the transfer of phosphate from creatine phosphate to ADP and supplementing thereby the store of mouse ATP, i.e.

$$^-OOC-CH_2-N(CH_3)-\underset{\underset{NH}{\|}}{C}-NH-\underset{\underset{^-O}{|}}{\overset{\overset{O}{\|}}{P}}-O^- + \text{ppA} \rightarrow {}^-OOC-CH_2-N(CH_3)-\underset{\underset{NH}{\|}}{C}-NH_2 + \text{pppA},$$

that not only the reactive derivatives with an aromatic spacer of the type (I, a–f) but also derivatives of aliphatic 2-chloroethylamines, for example

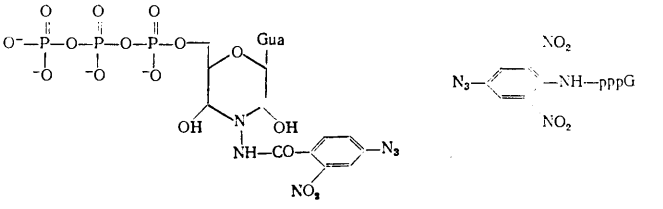
$$ClCH_2CH_2\diagdown\!\!\diagup N(H_3C)\text{—pppA}$$

are effective affinity reagents in relation to ATP-dependent enzymes.[69]

As already mentioned in Section III, the nucleoside 5′-trimetaphosphates are themselves affinity reagents. Apart from the RNA polymerase already mentioned, this has been demonstrated in relation to nucleotide-tRNA transferase[65] and phenylalanyl-tRNA synthetase from *E. coli*.[70]

The molecule of nucleotides are fairly large and the region of contact between the proteins "recognising" them can be fairly extensive. The data obtained with the aid of reagents without reactive groups in different parts of the molecule can therefore supplement significantly one another.

As an example, one may quote studies carried out with the protein elongation factor EF-G, which, combined in the complex with GTP, promotes the migration to the P site of the molecule of peptidyl-tRNA elongated by one aminoacid, formed on a ribosome via reaction (3) and present initially in the A site (such migration is necessary to make possible the start of the next peptide chain elongation cycle with selection of the next aminoacyl-tRNA molecule). In order that the EF-G factor should dissociate from the ribosome after such migration, it is necessary that the GTP molecule be hydrolysed to GDP and orthophosphate. Such activity is indeed characteristic of the complex of the ribosome and EF-G. However, in order to establish whether the corresponding catalytic centre is located on the ribosome or on the factor itself, it is important to determine where the GTP binding region is located. Experiments on affinity modification carried out with derivatives having reactive groups on the triphosphate fragment and on the ribosome residue have shown in both cases that the factor and not the ribosome is affinity labelled, i.e. that throughout most of its extent GTP is bound precisely to the factor:[57,71]



As a second example one may quote data obtained for ATP(CTP):tTNA-nucleotidyl-transferase. As can be seen from Schemes 5 and 6, this enzyme catalyses at least two reactions—the transfer of the CMP residue from CTP to the molecules of tRNA with an incomplete pCpC fragment and the transfer of AMP from ATP to tRNA with a complete pCpC fragment. It has not been established whether the enzyme has two different centres in order to effect these two reactions or whether all the events are played out at a single centre whose specificity changes depending on the nature of the tRNA end fragment. The use of periodate-oxidised ATP and CTP, namely oATP and oCTP, containing the dialdehyde groups in the modified ribose fragment, has shown that both compounds inactivate the enzyme. However, the employment of oATP leads predominantly to the inactivation of the enzyme in reaction (5), while oCTP inactivates reaction (6). These data show that CTP and ATP are located at least partially in different regions.[72]

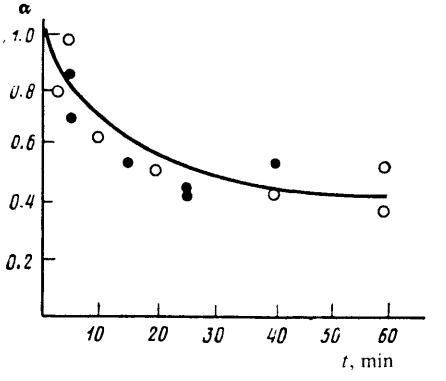


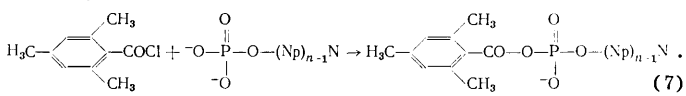
Figure 4. Kinetic curve for the inactivation of the tRNA-nucleotidyltransferase in the presence of 10^{-3} M reagent (If) at 37 °C: filled circles—residual activity determined from the incorporation of [^{3}H]AMP; open circles—ditto determined from the incorporation of [^{3}H]CMP in tRNA.[65]

On the other hand, studies carried out with the aid of the derivative (If) having an alkylating group bound to the γ-phosphate, and also with the aid of ATMP and CTMP have shown that the modification of the enzyme suppresses both activities to the same extent. As an example, Fig. 4 presents

the results of a study of the kinetics of the enzyme inactivation by the derivative (If) measured on the basis of the incorporation in tRNA of labelled AMP and CMP from which the pCpCpA end has been partly removed. Evidently, within the limits of experimental error, the data obtained by means of both tests agree. This result shows that, when derivatives with a reactive group on the triphosphate fragment are used, the group which is equally important for reactions (5) and (6) is attacked.[65]

V. REACTIVE DERIVATIVES OF OLIGONUCLEOTIDES

The first reactive derivatives of oligonucleotides were obtained by Grineva and co-workers in connection with the method for the complementarily addressed modification of nucleic acids which they developed.[73,74] The alkylating derivatives of oligonucleotides with a reactive group at the 3′-end were synthesised by reaction (4) which in broad outline proved to be suitable in this case also. The only significant modification on passing from monomers to short oligomers and longer oligonucleotides was the employment of Cetavlon salts of oligonucleotides in order to improve their solubility in dimethylformamide.[75] The method has also been applied to the more readily available deoxyribo-oligonucleotides with a 3′-terminal ribonucleotide fragment.[76] The reaction of *p*-(*N*-2-chloroethyl-*N*-methylamino)benzylamine ($ClRCH_2NH_2$) with the 5′-terminal phosphate group of the oligonucleotide in the presence of condensing agents has been developed for the synthesis of derivatives with an alkylating group at the 5′-end. The condensing reagents used were initially diphenyl phosphorochloridate[77] and later mesitoyl chloride, which leads to the formation of a mixed anhydride between the 5′-terminal phosphate and mesitylenecarboxylic acid:[78]



(7)

Treatment of the resulting mixed anhydride with the amine $ClRCH_2NH_2$ leads to the formation of the required product. When ribo-oligonucleotides are employed, these condensing agents have been shown[79–81] to produce intramolecular cyclic phosphotriesters with participation of the 2′-hydroxy-group, which hydrolyse in water with the partial cleavage of the internucleotide bonds and the isomerisation of the natural internucleotide 3′ → 5′ bond to the 2′ → 5′ bond. Recently such derivatives have been obtained predominantly using as the condensing agent a mixture of triphenylphosphine and dipyridyl disulphide,[30] which does not attack the internucleotide bond in the presence of highly basic amines.[82]

Many important characteristics of the complementarily addressed modification have been established with the aid of these reagents. It has been shown in relation to the reaction of ribosomal RNA from *E.coli*[83] that alkylation of the latter by derivatives of the oligoadenilates $(pA)_nCHRCl$ proceeds as a typical intracomplex reaction—the degree of modification of the ribosomes as a function of the reagent concentration reaches a plateau and does not increase on further increase of the excess of the reagent. In the presence of a small excess of the reagent, about 90% of the latter is consumed in the alkylation of the ribosomes, although, according to the competition factor for the intermediate ethyleneimmonium cations, this quantity should have been a fraction per cent if the reaction proceeded without the preliminary complex formation.[83] The composition of the alkylated bases changes sharply. Whereas the alkylation of tRNA by the analogous derivatives of uridine of the methyl ester of UMP results in the predominant or even exclusive alkylation of the guanine residues,[84,85] the reaction in the complex, where the direction of attack is determined primarily not by the relative reactivities of the bases but by their accessibility to the attack by the alkylating group, fairly rigidly fixed by the address, results in the alkylation of adenine, guanine, and cytosine to comparable extents.[86] Analogous results have been obtained in the study of the alkylation of DNA.[87,88] It has been shown in relation to the reaction of yeast valine tRNA (Fig.5) with the reagent dCpdGprACHRCl, which interacts with the C–G fragments of tRNA, that the fourth, reckoning from the complex formation section, residues in the direction of the 5′-end of the target molecule are alkylated.[89] Later these data were confirmed on a synthetic model:

(5′) d(pXpXpCpCpTpGpTpTpTpGpGpC) (3′)
(3′) ClRHC < rAd(CpApApApCpCpGpT) (5′)

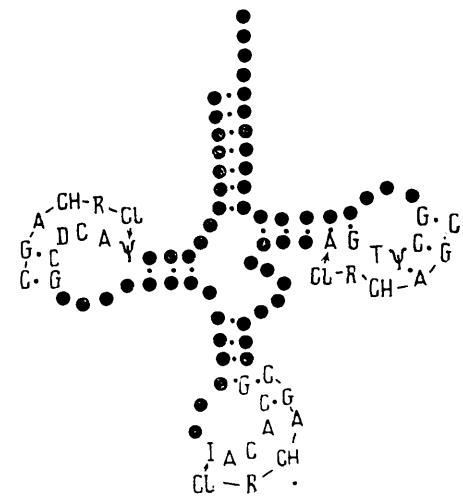


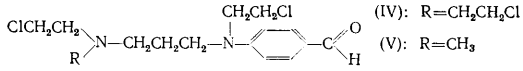
Figure 5. Specific alkylation by the complementarily addressed reagent dCpdGprACHRCl in the structure of the yeast valine tRNA;[89] the letters denote only the nucleotides in the reagent binding regions.

Here and in the next analogous scheme the symbol d is placed before the entire deoxyoligonucleotide sequence, rA denotes adenosine ribonucleoside, and the 5′- and 3′-ends of the two antiparallel complementary chains are indicated in brackets. In all the cases investigated only the d(pXpX) fragment was alkylated in the complex.[90]

Alkylation of DNA by oligonucleotide derivatives with subsequent cleavage at the alkylation points has been proposed as a general method for the selective cleavage of DNA at sections adjoining the nucleotide sequences complementary to the address.[91]

Several other methods for the introduction of reactive groups into the terminal fragments of oligonucleotides have been described. Thus, periodate oxidation followed by treatment with *N*-(4-azidobenzoyl)glycylhydrazide[92] and acylation of the *cis*-diol group with the imidazolide of *p*-azidobenzoic acid[93] have been used for the introduction of the photoactive arylazido-group at the 3′-terminal *cis*-diol.

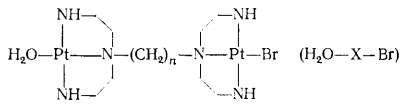
The introduction of an alkylating group into an oligonucleotide at the 5′-end via the alkylation with a trifunctional agent (IV),[42] in which the reactivity of one of the 2-chloroethylamino-groups is controllable, has been described:



(IV): R=CH_2CH_2Cl
(V): R=CH_3

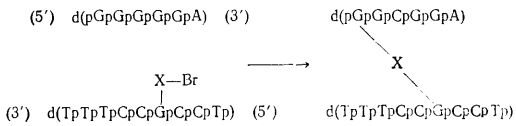
The phosphate is alkylated by the reactive aliphatic group (the second C—Cl bond is then hydrolysed) and the reactivity of the aromatic 2-chloroethylamino-group in the resulting derivative is then increased by reducing the formyl group to the hydroxymethyl group with sodium tetrahydroborate.[94]

The bifunctional platinum derivative[22]



(H_2O—X—Br)

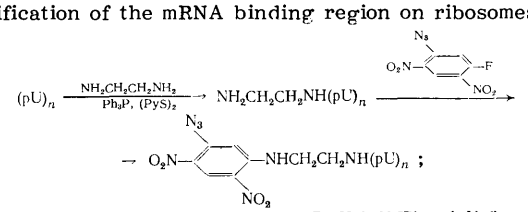
has been suggested for the introduction of reactive residues into the inner sections of an oligonucleotide. Water is readily substituted by the guanine residue in the oligonucleotide functioning as the address. The Pt—Br bond is significantly stronger and reacts with nucleic acid bases only under the conditions of a stable contact generated by a complementary complex. Complementarily addressed modification in a complex has been achieved in this way and, among the four guanine groups of the target oligonucleotide, only one, located in the position within the complex most favourable for the reaction, proved to have been modified:



Derivatives of oligonucleotides having the dimethylaminonaphthalenesulphonyl (dansyl, DNS) residue have been obtained. It has been shown in relation to the derivative DNS-$NHCH_2CH_2(pT)_9$ [95] that, in the two-quantum excitation by means of a laser having a wavelength of 337 nm, the polyadenylic acid complementary to the address is cleaved in the presence of this reagent, but polyuridylic and polycytidylic acids are not cleaved under these conditions.

The addition of a chelating fragment, namely ethylenediaminetetra-acetic acid, to an oligothymidylate has also been achieved. In the presence of Fe^{2+} and O_2 this derivative cleaves the complementary polyadenylate and, to a significantly lesser extent, non-complementary polynucleotides.[96]

In many cases a special group, by means of which it is possible to carry out a highly selective reaction with a heterobifunctional reagent containing the future reactive fragment of the addressed reagent, is introduced beforehand to reactive oligonucleotide derivatives in the course of their synthesis. Aliphatic or aromatic amino-groups, which can be introduced either at the terminal phosphate[97–99] or into the heterocyclic base, for example, in the synthesis of an oligonucleotide containing 5-aminouracil instead of one of the uracil residues,[100] are used for this purpose. As an example, one may quote derivatives employed for the affinity modification of the mRNA binding region on ribosomes:



NH_2Ph—pApUpG + $(BrCH_2CO)_2O$ → $BrCH_2CONHPh$—pApUpG ;
UpUpUp(5-NH_2)U + ICH_2COCl → UpUpUp (5-ICH_2CONH)U .

Derivatives in which the terminal phosphate has been replaced by the phosphorothioate residue have been proposed for the same purpose. In particular, derivatives of deoxyoligoribonucleotides have been obtained in this way by alkylating phosphorothioates with reagents (IV) or (V) with subsequent activation of the aromatic 2-chloroethylamino-group via its reduction with tetrahydroborate.[101,102]

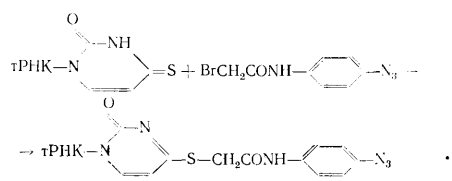
A novel method of synthesis of reactive derivatives of oligoribonucleotides has been proposed.[6,103] It is based on the substrate activity of γ-derivatives of nucleoside 5′-triphosphates in a reaction catalysed by RNA polymerase. In the synthesis of RNA on a DNA template using instead of the natural substrate its derivative with a reactive group, a product retaining this group at the 5′-end has been obtained:

$N_3PhNHpppA \xrightarrow{pppU} N_3PhNHpppApU \xrightarrow{pppC} N_3PhNHpppApUpC \rightarrow \ldots$

In certain cases reactive derivatives can be obtained by the appropriate treatment of the complex of the oligonucleotide or its derivative with the biopolymer. Thus the affinity modification of the mRNA binding region has been achieved[104] by treating the complex of the ribosomes of *E.coli* with the phenylalanine tRNA and $pp(pU)_7$ with water-soluble carbodiimide, which converts the terminal triphosphate group into a trimetaphosphate group.

VI. REACTIVE DERIVATIVES OF NUCLEIC ACIDS

The greatest number of reactive derivatives have now been described for transfer RNA in connection with the study of their interaction with ribosomes and aminoacyl-tRNA synthetases. A list of the derivatives synthesised can be found in other reviews.[105,106] Their greatest number has been obtained by the addition of the corresponding heterobifunctional reagents directly to the *cis*-diol group, for example, via reaction (4),[107] or with preliminary oxidation by periodate, and via the α-amino-group of aminoacyl tRNA. Compounds (II) and (III) are examples of such derivatives. The first affinity modification of ribosomes has been achieved with the aid of compound (II), first described by Grachev and Ryvkin,[108] and information has been obtained about the location of the peptidyl-transferase centre.[109] The selective addition of bifunctional reagents to certain so-called minor bases, which are present in large amounts in tRNA, has also been employed. Thus the presence of 4-thiouridine in the 8-position relative to the 5′-end is characteristic of the tRNA from *E.coli* and the 4-thiouridine group can be selectively alkylated by a reagent with an aryl azide group:[9]



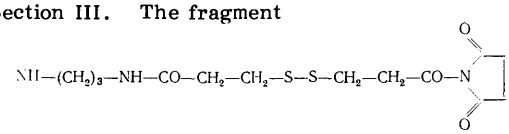
The method of direct photo cross-linking has also been used in the study of the interaction of tRNA with aminoacyl-tRNA synthetases.[110] A detailed analysis of the data obtained by this method can be found in the paper of Remy and co-workers in Knorre's monograph.[3] It must be emphasised that ultraviolet irradiation in the region of 260 nm damages significantly nucleic acids and proteins and the results obtained by the method of direct photo cross-linking must be treated with much caution. The method is undoubtedly attractive because of its simplicity and the absence of any perturbations to the ligand before the instant of elimination and the possibility of carrying out the process very rapidly using powerful light

pulses. However, as already stated, a detailed preliminary study of the reactions occurring and of the properties of the photo cross-linking products formed is required.

Methods based on the selective excitation of certain specific chromophores present in tRNA as minor components and absorbing in the long-wavelength ultraviolet part of the spectrum, sufficiently remote from the region corresponding to absorption by the remaining bases and proteins, are nowadays more attractive. An example of such a group is 4-thiouridine already mentioned. It has been shown[9] that irradiation of phenylalanine tRNA from *E.coli* in a complex with phenylalanyl-tRNA synthetase leads to the cross-linking of these two macromolecules. According to the data of Ofengand and Liou,[111] the tRNA containing in the 5'-position in the codon a uridine derivative (5-carboxymethoxyuridine), in a ternary complex with a ribosome and mRNA, is cross-linked on ultraviolet irradiation with the pRNA of the small subunit of the ribosome. The irradiation of ribosomes in a complex with yeast phenylalanine tRNA and polyuridilic acid leads to the cross-linking of the latter with the nucleoside wybutosine adjoining the anticodon from the 3'-end.[112]

As already stated in Section III, many problems of the protein–nucleic acid recognition and of the specific action on nucleic acids can be solved using derivatives of polynucleotides and nucleic acids in which reactive groups have been introduced statistically. Polynucleotides of this type can be obtained by copolymerisation with monomers containing chemically reactive groups. Thus the copolymerisation of ADP with 8-azido-ADP and of inosine 5'-diphosphate with 8-azidoinosine diphosphate has been described.[113] The copolymers obtained were used for the affinity modification of the RNA polymerase from *E.coli*.

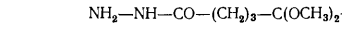
Derivatives of phenylalanine tRNA from *E.coli* with statistically attached aryl azide groups have already been described in Section III. The fragment



with acylating activity has been introduced statistically[114] into accessible (not involved in the formation of the secondary structure) cytosine residues of the initiator methionine tRNA from *E.coli*. The derivative obtained was used for the affinity modification of methionyl-tRNA synthetase from the same source. The presence of the S–S bridge makes it possible to split off tRNA from the protein by treatment with thiols after the affinity modification. 4-Thiouracil residues, formed from cytosine residues on treatment of tRNA with hydrogen sulphide, have been introduced statistically into the same tRNA by treatment with hydrogen sulphide. The photoaffinity modification of ribosomes has been achieved with the aid of such tRNA.[115]

The use of the T7 phage mRNA, containing alkylating groups introduced by treating the mRNA with reagent (IV), for specific mutagenesis involving specific genes has been described.[116,117] Analogous derivatives have been obtained from the DNA fragment containing the gene imparting resistance to tetracycline.[118] These reagents have been used for the specific induction of mutations in the pBR 322 plasmid, widely used in gene engineering studies. Although all the experiments have been carried out with isolated phage and plasmid DNA, it is evident that this approach leads to prospects for mutagenesis in living organisms, directed to specific genes, as well as to the prospect for the blocking of the operation of specific genes. The statistical character of the distribution of the reactive groups in the solution of such problems is especially significant, since it is not known beforehand into which points within the gene it is necessary to introduce modifications in order to obtain interesting mutations or in order to switch off its operation.

The initial idea has been realised in a study[119] in which the cytosine residues in the T7 phage mRNA were modified by the reagent



After the introduction of the reagent at the cytosine groups of the address, it was activated by acid treatment, which converts the ketal into a ketone, enhancing thereby the electrophilic character of the C–Br bond. The statistical introduction of aldehyde groups into DNA forming part of the composition of chromatin was achieved by treatment with dimethyl sulphate and subsequent splitting off of 7-methylguanine groups. The aldehyde groups readily form Schiff bases with the amino-groups of the chromatin proteins in contact with them. Treatment with sodium tetrahydroborate leads to the formation of stable alkylamines, i.e. to the covalent binding of DNA to the proteins. Analysis of the reaction products make it possible to obtain important information about the structural organisation of nucleosomes—the nucleoprotein complexes in which the DNA in the cells of higher organisms is packed.[120]

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The data presented in the review show that organic and bio-organic chemistry have armed investigators with a large arsenal of fine chemical instruments for the study of the problem of the protein–nucleic acid recognition and the development of fundamentally new approaches to influencing the genetic apparatus in living organisms. The number of reactive derivatives of nucleic acids and their components known at the present time is so large that the present authors have been unable to describe or even list all such derivatives and were forced to confine themselves to the description of the principal types. On the other hand, the methodology of the application of these instruments to the purpose of research still requires profound physicochemical and biochemical investigations. The authors believe that the most acute problems include the study of the mechanisms of the reactions used for the affinity modification of biopolymers and also the study by modern physical methods of the structures of the complexes of biopolymers with affinity reagents and the structures of the products formed. Such investigations have now become possible in relation to derivatives not only of nucleotides but also of those of oligonucleotides, which is a result of impressive advances in the field of their chemical synthesis.

Complexes of derivatives of oligonucleotides with complementary oligonucleotides and nucleic acids are unique models for the study of the general characteristics of their intracomplex reactions, modelling in their specificity natural enzymic reactions. In fact a new field of bio-organic chemistry, namely the organic chemistry of nucleic acid duplexes, has already begun to form.[121]

The possibility of obtaining oligonucleotides and their derivatives in amounts running into tens and hundreds of milligrams makes it possible to begin systematic studies on such derivatives of biologically active substances. The possibility of establishing the primary structure of virtually any nucleic acids ensures the specific synthesis of oligo- and poly-nucleotide addresses for the most varied sections of the genetic apparatus in living organisms and the development on this basis of methods whereby biological objects can be influenced, which are superior in their selectivity to other chemical methods and approach, in terms of the level of their selectivity, the most sophisticated antibiotics and

enzymes. The authors hope that this review will attract the attention of chemists involved in the most varied disciplines (organic and inorganic chemists, physical chemists, and analytical chemists) to this new vigorously developing field of science, which has extremely attractive prospects.

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The Applications and Prospects for Further Applications of Biocatalysts in Electrochemical Systems

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A new field involving the use of biologically active substances for the acceleration of electrode processes is examined. The coupling of enzymic and electrochemical reactions can be achieved in two ways: by mediated and direct electron exchange between the active centre of the enzyme and the electrode. The mechanism of the electrochemical oxidation of hydrogen with participation of immobilised hydrogenases is analysed in detail. Data indicating a tunnel mechanism of electron transport in the enzyme catalysis of electrode processes are presented. The principal applications of bioelectrochemical systems are indicated: as analytical sensors, as bioelectrochemical energy converters, and in bioelectrosynthesis.
The bibliography includes 129 references.

CONTENTS

I. Introduction 852
II. Methods for the coupling of enzymic and electrochemical reactions in bioelectrocatalysis 852
III. Principal applications of bioelectrocatalytic systems 858

I. INTRODUCTION

The field of bioelectrochemical research has two main components. The first involves the study of membrane phenomena, which are extremely common in living nature. Its main feature is the study of the properties of membranes, including membranes with incorporated enzyme systems. This is of considerable interest for the understanding of the energy conversion process and electron transport in living organisms. The second component in bioelectrochemistry is the use of biological systems as catalysts of electrode reactions. Its development is due to the high specificity and efficiency of enzymic reactions and also the possibility of their occurrence under mild conditions.

Biocatalysts can be employed to create electrochemical analytical devices, in the development of electrochemical energy converters, in the specific electrosynthesis of complex organic compounds, and also for the elucidation of the mechanisms of enzyme reactions by electrochemical methods.

At the present time one can speak of bioelectrocatalysis as a phenomenon involving the acceleration of electrode processes under the influence of biocatalysts.[1] The study of bioelectrocatalysis implies in the first place the study of the methods of coupling enzymic and electrochemical reactions and also of the mechanism of electron transport in the enzyme–electrode system.

The aim of the present study was to demonstrate the advances and prospects in this new branch of chemical research.

II. METHODS FOR THE COUPLING OF ENZYMIC AND ELECTROCHEMICAL REACTIONS IN BIOELECTROCATALYSIS

1. Electron Transport Using a Mediator

The coupling of enzymic and electrochemical reactions by means of a mediator can be achieved mainly in three ways, which differ in the mobility of the mediator and enzyme in relation to the electrode surface (Fig.1): (a) the enzyme and the mediator are in the bulk of the solution and the mediator diffuses to the electrode surface; (b) the enzyme is immobilised on the electrode surface and the mediator is in the bulk of the solution; (c) the enzyme and the mediator are immobilised on the electrode surface.

The mediator is as a rule either an electrochemically active product of the enzymic reaction or a transferring agent specially selected for the given system. The use of chemical compounds as mediators for the coupling of specific enzymic and electrochemical reactions imposes specific requirements which must be met by such transferring agents and which have been formulated.[2,3]

1. The stage involving the interaction of the mediator with the active centre of the enzyme must be rapid, i.e. the mediator must be a specific substrate of the enzyme.

2. The normal oxidation-reduction potential of the mediator must be close to that of the fuel of the oxidant. It is especially important that this condition be fulfilled in the development of electrochemical energy generators, since otherwise the efficiency of such systems diminishes. On the other hand, a transferring agent with a low oxidation-reduction potential is readily oxidised by oxygen, which is particularly undesirable when enzymes are used in electrochemical analytical devices.

3. The mediator must be electrochemically oxidised or reduced at the electrode of the given material under conditions close to reversibility.

4. The mediator system must be stable.

One of the first studies on bioelectrocatalysis was devoted to the catalytic properties of the enzyme hydrogenase in the electrochemical oxidation of hydrogen. The aim of these studies was to create the hydrogen anode of a fuel cell,[4-7] to determine the hydrogenase activity,[8,9] or to investigate the possibility of the electrochemical evolution of hydrogen in the presence of the enzyme.[10]

The possibility of creating a fuel cell anode on the basis of the *E.coli* hydrogenase has been examined.[4] The methylene blue–leuco-methylene blue system, which has an oxidation-reduction potential of +0.01 V relative to the hydrogen electrode (at pH 7.0), was used as the diffusionally mobile transferring agent. In this system methylene blue is enzymatically reduced by hydrogen to the leuco-form, which is then reoxidised at the platinum electrode. The maximum current density at the anode is 0.16 mA cm^{-2}.

The formation of hydrogen from the protons by the reduction of methylviologen in the presence of hydrogenase has been investigated by Yagi.[10] The reversibility of this system

with respect to hydrogen was demonstrated in this way.

It has been shown[1,2,3,11] that the optimum transferring agent for the hydrogen–hydrogenase–electrode system is methylviologen, whose oxidation-reduction potential is close to the reversible hydrogen electrode potential at a pH close to neutrality. It was established that, when the hydrogenases from *Thiocapsa roseopersicina* and *Pseudomonas aestuarii* are used for the anodic oxidation of hydrogen in the H_2–enzyme–methylviologen–carbon electrode system, it is possible to achieve this reaction under conditions close to reversibility.

The systems examined above contain the enzyme and the mediator in solution. From the practical point of view a system in which at least one of the components is on the electrode surface are more convenient.

The system for the oxidation of hydrogen based on hydrogenase and methylviologen as the mediator can serve as an example of the systems where the enzyme is immobilised on the electrode surface and the mediator is diffusionally mobile.[12] The authors developed a method for the adsorption immobilisation of hydrogenase on the surface of a carbon black electrode with a specific surface of ~100 $m^2\ g^{-1}$. The hydrogenase is adsorbed on the carbon black irreversibly and retains approximately 90% of the activity of the native enzyme. The enzymic reaction occurring in the immediate vicinity of the electrode surface in the presence of methylviologen and hydrogen results in the formation of the reduced form of the mediator, which can be reoxidised at the electrode or can diffuse into the bulk of the solution, the relative contributions of these processes depending on the electrode potential. The studies were carried out by the method involving the use of semi-immersed and rotating disc electrodes. The results obtained show that, in the presence of a sufficiently active enzyme, the reaction is controlled not only by the kinetics of the oxidation of hydrogen but also by the diffusion of the latter to the electrode surface. At a potential of −0.15 V and a methylviologen concentration of 8×10^{-3} M the current density at the electrodes was 1.1–1.2 mA cm^{-2}.

A number of studies have been devoted to the development of a biocathode for the fuel cell. The hydrogen electrochemical reduction reaction on carbonaceous materials in neutral solutions proceeds with a high overpotential. It has been suggested that a mediator enzyme system be used to activate this reaction.[13–16] The oxidation-reduction potential of the transferring agents in such systems is more positive than the range of potentials in which oxygen is electrochemically reduced on the carbon electrode. The cytochrome *c* oxidase–*NNN'N'*-tetramethyl-*p*-phenylenediamine (TMPD) system has been used,[18] TMPD being oxidised by the enzyme to a radical (Wurster's Blue) and the latter being reduced at the cathode. This mediator can be oxidised by oxygen also in the absence of a catalyst, but in the presence of cytochrome *c* oxidase the rate of this reaction greatly increases. It has been shown that TMPD–Wurster's Blue system is electrochemically reversible at the platinum and graphite electrodes and that its redox potential is 0.7 V.

The transferring system incorporating 4,4'-dihydroxybiphenyl and its oxidised form has also been used in the cathodic reduction of oxygen in the presence of laccase.[17] These mediators were resorted to in connection with the search for a system of transferring agents whose oxidation-reduction potential is close to the equilibrium potential of the oxygen electrode. Potato *o*-diphenol oxidase has been used to accelerate the oxygen electrochemical reduction reaction.[18] The mediators were catechol and caffeic and chlorogenic acids. The authors were able to shift the oxygen electrochemical reduction potential into the positive region by 300–350 mV.

NAD- and NADP-dependent enzymes play a major role in metabolic processes. Bioanodes employing dehydrogenases and the NAD–NADH redox transferring system have been described.[18–20] A disadvantage of these systems is the occurence of irreversible processes: frequent repetition of the electrochemical reaction lead, in particular, to the dimerisation of the transferring agent. In addition, the electrochemical NADH oxidation and NAD reduction processes proceed with a high overpotential. It has been shown[20] that the electrochemical oxidation of NADH on smooth and platinised platinum and also on pyrographite proceeds only at a potential above +1.3 V (relative to the normal hydrogen electrode). In the presence of phenazine metasulphate, the NADH oxidation potential at the pyrographite electrode falls to +0.4 V. The authors[20] describe the electrochemical oxidation of sodium formate at the pyrographite electrode in a system with the NAD-dependent formate dehydrogenase using phenazine methosulphate as the mediator and also using a two-enzyme system with an NAD-dependent formate dehydrogenase and an NADH-dependent dehydrogenase, where methylviologen is the electron transferring agent. The sodium formate oxidation currents in the given system at a potential above +0.2 V were 15 mA cm^{-2}. Systems in which the enzyme and the mediator are simultaneously immobilised

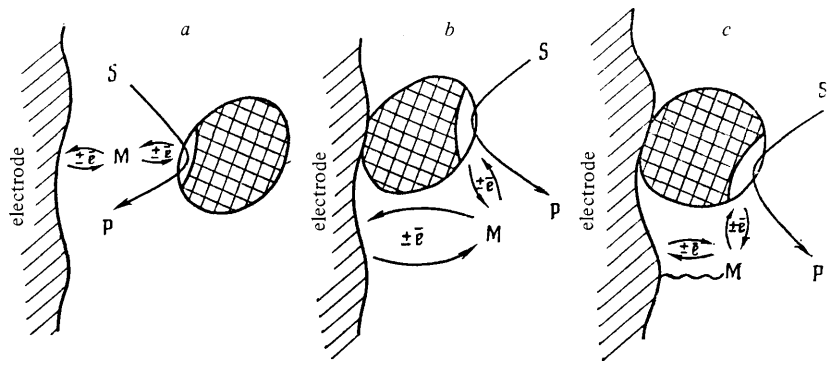


Figure 1. Schematic illustration of the possible ways of coupling enzymic and electrochemical reactions with the aid of a mediator; S = substrate, P = product of enzymic reaction; M = electron transferring agent (for the description of the schemes, see text).

on the electrode surface are superior to those described above. The possibility of creating a model of the enzyme fuel cell, using alcohol as the fuel, and also of devising an analytical electrochemical sensor for alcohol has been investigated.[21,22]. The alcohol oxidation catalyst was horse liver alcohol dehydrogenase and the mediator was nicotinamide-adenine dinucleotide. The enzyme and the cofactor were immobilised on the electrode surface in two ways: by adsorption via the hydrophobic and electrostatic interactions of the enzyme–cofactor system with the electrically conducting carrier and covalently by grafting NAD to the carrier and by sorbing the apoenzyme on the cofactor. It has been shown that the cofactor retains its physiological activity only when it is separated from the carrier by a distance of ~10 Å. When the enzyme and NAD were introduced into the cell, a stable current and e.m.f. were generated. The introduction of a small amount of potassium cyanide, which is an inhibitor of the enzyme activity of alcohol dehydrogenase (ADH), into the electrolyte reduced the current. The current was proportional to the substrate concentration and reached a maximum of 0.6 mA at a potential of 0.2 V.

Yastrebova et al.[23] also used the ADH–NAD enzyme–cofactor complex immobilised on the surface of a carbon black electrode as the mediator in the electrochemical oxidation of ethanol. The half-wave potential $E_{1/2}$ in the oxidation of NADH in the enzyme–cofactor complex is then lower by 0.22 V than $E_{1/2}$ for the oxidation of NADH adsorbed on the carbon black. The direct involvement of the enzyme in the electrochemical oxidation of NADH was confirmed by adding an ADH inhibitor (phenanthroline) to the adsorbed complex, which resulted in the disappearance of the catalytic effect. A mechanism for the oxidation of ethanol at the enzyme electrode has been proposed. The method suggested makes it possible not only to determine ethanol in the concentration range 3×10^{-5}–5×10^{-4} M but also to regenerate the NAD coenzyme using ADH. ADH and the following mediators have been employed[24] for the oxidation of ethanol: methylene blue and the *N*-methylphenazine ion, which oxidise NADH, are produced by the reduction of NAD due to the occurrence of the enzymic reaction and are themselves oxidised at the electrode. The anodic compartment of the electrochemical cell employed contained the enzyme methanol dehydrogenase, which oxidises methanol, according to the data of Varfolomeev et al.[2] in the presence of phenazine methosulphate and phenazine ethosulphate as mediators. The maximum current in the system reached 3.7 mA.

The FAD-dependent enzymes glucose oxidase and amino-acid oxidases belong to the group of enzymes which play a significant role in oxidation-reduction processes in living organisms. L-Aminoacid oxidase, bound covalently to the surface of a carbon black electrode modified with 2,4,6-trichlorotriazine, has been used[26] to determine L-aminoacids. The electrode potential varies linearly with the aminoacid concentration in the range 10^{-5}–10^{-2} M.

The study of the electrochemical oxidation of glucose in the presence of bio-organic catalysts is of great interest because this reaction takes place on platinum with a high overpotential. A carbon electrode modified with 2,4,6-trichlorotriazine with the covalently attached enzyme has been used[27] in the study of the reduction of glucose oxidase, which occurred at a potential of −0.51 V (relative to the Ag/AgCl electrode), which is more positive by 100 mV than in the reduction of the apoenzyme. The enzymic oxidation of glucose on a vitreous carbon electrode with adsorbed mediators has been investigated.[28] Glucose oxidase was deposited on the modified electrode and was separated from the bulk of the solution by a dialysis membrane. The transferring agents were tetracyano-*p*-quinodimethane and the potassium salt of its anion, pyocyanin, 9,10-phenanthrenequinone, dichlorophenol-indophenol, and dextran-dopamine. These compounds are substrates of glucose oxidase. The maximum current in the system depended on the concentrations of the components in the layer near the electrode and on the nature of the transferring agent, reaching 67 μA cm^{-2} under anaerobic conditions. The electrochemical oxidation of glucose has been investigated[29,30] in the presence of glucose oxidase immobilised on organic metals—the complexes of *N*-methylphenazinium (HMP^+) and *N*-methylacridinium (HMA^+) ions with the tetracyanoquinodimethane radical-ion. The biocatalytic effect occurred at potentials in excess of −0.05 V (Ag/AgCl). The dependence of the current on the glucose concentration was described by a curve with saturation, the limiting current depending on the electrode potential. The electrode with the immobilised enzyme retains its activity for more than 100 days.

Metalloenzymes, containing iron and copper ions in their molecule, play a major role in electron transport in biological systems. The cytochrome b_2–potassium hexacyanoferrate(III)/hexacyanoferrate(II) system has been used to activate the lactate oxidation reaction on the platinum electrode.[31,32] Studies were performed in a two-electrode cell whose anodic and cathodic compartments were separated by an electrically conducting bridge. A solution of the lactate, potassium hexacyanoferrate(III), and the enzyme was placed in the anodic compartment, while a solution of potassium hexacyanoferrate(III) was placed in the cathodic compartment. The enzymic reaction resulted in the formation of hexacyanoferrate(II), which was then electrochemically oxidised at the anode. The hexacyanoferrate(III) was electrochemically reduced at the cathode. The current in the external circuit when the cell was switched on varied linearly with the lactate concentration in the range from 5×10^{-6} to 4×10^{-3} M. 2,6-Dichlorophenol-indophenol, phenazine methosulphate, methylene blue, and indigocarmine have also been used as transferring agents. Johnson and co-workers[33,34] employed a mediator system to control the potential in the layer containing the enzyme galactose oxidase. In the course of the enzymic reaction, the active centre is reduced and then reversibly reoxidised by the mediator. The choice of the transferring agent is of decisive importance for the establishment of the appropriate potential in the system. Hexacyanoferrate(III), 2,6-dichlorophenol-indophenol, tetracyanomonophenanthroline ferrate, and tripyridinecobalt were used as the mediators.

As can be seen from the data presented, the mediator method of coupling the enzymic and electrochemical reactions using soluble mediators has been studied in fair detail. A new superior procedure for mediated transport, using transferring agents and enzymes in an immobilised state on electrodes as well as the direct electron exchange between the active centres of enzymes and the electrode, are of interest.

2. Electrochemical Reactions of Proteins on Electrodes

In connection with the possibility of using enzymes in electrocatalytic processes, the study of the electrochemical properties of proteins is of interest. The application of electrochemical research methods can yield important information about the mechanism of electron transfer in protein molecules and about the relation between the rate of electron transfer (or the rate of change of potential) and the conformational rearrangements of proteins.

The adsorption of proteins on the surfaces of electrodes plays a major role in the study of their electrochemical reactions. The adsorption of proteins on mercury electrodes and

the mechanism of electron transfer in such systems have been investigated by Kuznetsov and co-workers.[35-37] It has been shown that protein is rapidly adsorbed on the surface of mercury with formation of a monolayer of the denatured protein 8–10 Å thick. This protein layer is adsorbed irreversibly and covers approximately 80% of the mercury surface, forming a porous structure. The active centre of the denatured protein does not participate in electron exchange with the protein molecules in solution. The latter exchange electrons with the electrode through the pores in the irreversibly sorbed protein.

It is believed,[38] however, that, owing to the high surface pressure, the adsorbed molecules in the first monolayer on the mercury electrode are not denatured.

It has been shown that horse heart cytochrome *c* is reduced irreversibly on mercury.[39-42] The anodic potential scan does not show oxidation of the reduced protein. Cytochrome *c* is reduced with an overpotential[42] and the reduction process depends on the pH, the ionic strength of the solution, and the protein concentration.

Study of the behaviour of cytochrome *c* on a gold electrode modified with γγ-bipyridyl and 1,2-bis(4-pyridyl)ethylene showed that the prosthetic group of the protein undergoes reversible oxidation-reduction in the given system. It is of interest that modification of the lysine residues of cytochrome *c* causes cytochrome *c* to cease being a substrate of cytochrome *c* oxidases and at the same time the reversible electrochemical oxidation-reduction of the protein on the electrode stops.[43-48] The reversible oxidation-reduction of cytochrome *c* at the equilibrium potential has also been observed on a tin-doped indium oxide electrode[49] and a gold electrode modified with 1,2-bis(4-pyridyl)ethylene.[47] The oxidation-reduction rate constant on electrodes of this type is 0.014–0.019 cm s^{-1}.

Saponeva et al.[50] and Czochralska et al.[51] investigated the reduction of bacteriorhodopsin on mercury and platinum electrodes. The electrochemical behaviour of proteins has been examined in detail in a review.[52]

The proteins investigated[35-51] do not exhibit enzyme activity and behave solely as electron or oxygen transferring agents. The possibility of direct electron transfer to the active centres of enzymes in the absence of substrates has been investigated for xanthine oxidase,[53] lactate dehydrogenase,[54] catalase and superoxide dimutase,[55] peroxidase,[56] cholesterol oxidase,[57] and glucose oxidase.[58]

The haemin in the peroxidase molecule is electrochemically inactive on an amalgamated gold electrode and on gold and pyrographite electrodes. The reversible oxidation-reduction process observed on the gold amalgam corresponds to a reaction involving the S–S bonds.[56]

The electrochemical properties of cytochrome P-450 have been investigated[39] and it has been shown that cytochrome P-450 is reduced by mercury irreversibly at a potential of −1.4 V. Flavin-adenine dinucleotide (FAD), which forms part of the composition of the active centre of xanthine oxidase and D-aminoacid oxidase, is reduced on mercury in the range of potentials corresponding to free FAD.[36] The prosthetic group of another FAD-dependent enzyme, namely glucose oxidase, is reduced at the equilibrium oxidation-reduction potential of the enzyme.[58] The reversible oxidation-reduction on the mercury electrode of the prosthetic group of cholesterol oxidase, in which FAD is bound covalently to the apoenzyme has been observed, but it takes place with an overpotential.[57] One must note that the oxidation-reduction processes associated with the prosthetic groups of enzymes cannot indicate unambiguously the possibility of the effective electrocatalysis of the corresponding reactions by these enzymes, i.e. the redox reactions of the prosthetic groups in homogeneous enzyme catalysis differ from the corresponding redox reactions of the same groups in electrochemical systems. For example, peroxidase, in which the reduction of haemin has not been observed under anaerobic conditions,[56] is an effective catalyst of the electrochemical reduction of hydrogen peroxide. This effect will be discussed in detail below.

3. Direct Electron Transfer Between the Active Centre of the Enzyme and the Electrode

A fundamental problem in bioelectrocatalysis is that of the direct coupling of the enzymic and electrode reactions. The possibility of the direct electron transfer from the electrode to the active centre of the enzyme (or conversely) has been discussed.[11]

The preparation of effective catalysts of the electrochemical reduction of oxygen is of great practical importance. It is known that a steady-state potential established in an oxygen atmosphere for electrodes made of carbonaceous materials is far from the equilibrium oxygen potential and amounts to ~0.6–0.7 V. Cytochrome *c* has been used[59,60] as the catalyst of this reaction. It has been shown that the catalysis by cytochrome *c* occurs only in the adsorbed state over the entire experimental range of potentials (from −0.18 to +0.6 V). It has been established that in the presence of the biocatalyst not only does the rate of reduction of oxygen to hydrogen peroxide, i.e.

$$O_2 + 2\bar{e} + 2H^+ \rightarrow H_2O_2,$$

increase but also the parallel reaction involving its reduction to water occurs

$$O_2 + 4\bar{e} + 4H^+ \rightarrow 2H_2O.$$

The second reaction is associated with the rupture of the oxygen–oxygen bond and apparently proceeds via the adsorption of the oxygen molecules on the central iron atom in the active centre of cytochrome *c*.

A group of Japanese workers[61] established that cytochrome c_3 from *Desulfovibrio vulgaris* catalyses the reduction of molecular oxygen in the adsorbed state on the mercury electrode. In this case oxygen was fully reduced to water, i.e. via a four-electron mechanism without the formation of hydrogen peroxide. The maximum acceleration of the reaction was observed when the mercury electrode surface was 50% filled by the adsorbed cytochrome c_3.

The electrochemical reduction of oxygen and the direct electron transfer in the oxygen–*Polyporus versicolor* laccase–carbon electrode system has been studied in detail.[62,63] The enzyme was present on the surface of electrodes in the adsorbed state. The introduction of laccase into the system shifts the steady-state electrode potential towards positive values and accelerates the electrochemical reduction of O_2 in the potential range 1.2–0.6 V, the potentials and currents at the given potentials increasing with increase of the amount of enzyme adsorbed on the electrode. Gold, pyrographite, vitreous carbon, and carbon black were used as the electrode materials. The studies were performed under aerobic and anaerobic conditions. The maximum potential of +1.207 V was established in an oxygen atmosphere for electrodes which had been kept beforehand in a solution of laccase at a concentration of ~10^{-5} M for 24 h. The introduction of a laccase inhibitor into the system (F^- or N_3^- ions) virtually stopped the acceleration of the electrochemical reduction of oxygen (Fig.2). The stable and reproducible potential of +1.20 V permitted a detailed investigation of the mechanism of the electrochemical reduction of oxygen in the vicinity of the

equilibrium potential. The linear relation between the current and the overpotential is maintained in the potential range 1.20–1.15 V. In the potential range 1.18–1.15 V the slope of the polarisation curve increases up to $\partial E/\partial \lg i \cong 0.03$ V. At potentials more negative than 1.15 V, we have $\partial E/\partial \lg i \cong 0.06$ V. Along the 1.20–1.15 V section of the polarisation curve, $\partial E/\partial \lg i \cong \partial E/\partial \lg p_{O_2}$, i.e. the reaction is of first order with respect to oxygen and the dependence on pH is given by $\partial E/\partial \mathrm{pH} \cong 0.06$ V. The calculated stoichiometric number was found to range from 0.75 to 1.8 with an average of 1.2. Consequently, the slow stage in the electrochemical reduction of oxygen is repeated once. On the basis of the experimental data, the authors proposed a mechanism for the electrochemical reduction of oxygen in the presence of laccase:

$$\begin{gathered}
E + O_2 \rightleftharpoons EO_2, \\
EO_2 + \bar{e} \rightleftharpoons EO_2^-, \\
EO_2^- + H^+ \rightleftharpoons EO_2H, \\
EO_2H + 2\bar{e} + H^+ \rightarrow EO^- + H_2O \ (E = 1{,}2 \div 1.15\mathrm{V}), \\
EO^- + \bar{e} + H^+ \rightleftharpoons EOH^-, \\
EOH^- + H^+ \rightleftharpoons E + H_2O, \\
\hline
O_2 + 4\bar{e} + 4H \rightleftharpoons 2H_2O,
\end{gathered}$$

where E is the enzyme.

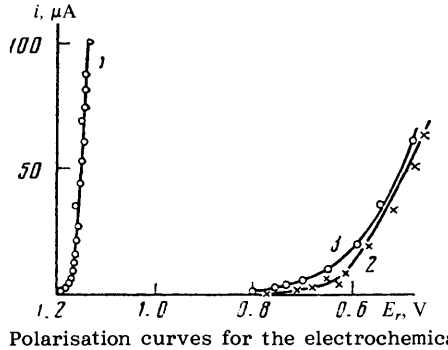


Figure 2. Polarisation curves for the electrochemical reduction of oxygen at an electrode with immobilised laccase: 1) in an oxygen atmosphere; 2) in the presence of the N_3^- inhibitor; 3) background curve in the absence of enzyme.

The synchronous transfer of two electrons in the slow stage is unusual for an electrochemical reaction. However, the authors postulate that the presence of a two-electron acceptor in the laccase molecule makes it possible to achieve this reaction.

The non-mediated catalysis of the electrochemical reduction of oxygen using potato *o*-diphenol : oxidoreductase has been investigated.[16] In the presence of the enzyme adsorbed on the carbon black electrode, a potential of +1.13–1.16 V is established in an oxygen atmosphere. It has been shown using a disc electrode with a ring that, as for the electrode with laccase, oxygen is reduced directly to water in the given system without the formation of H_2O_2.

The electrochemical oxidation of hydrogen in the presence of hydrogenase is of considerable interest in connection with the search for new non-metallic catalysts for the hydrogen electrode of the fuel cell. Results indicating the possibility of the direct oxidation of H_2 at carbon black electrodes by the hydrogenase from *Thiocapsa roseopersicina* immobilised by adsorption have been obtained.[64] The equilibrium hydrogen potential has been realised at these electrodes. Analysis of the kinetic parameters of the system led to the following mechanism of the electrochemical oxidation of hydrogen:

$$\begin{gathered}
E + H_2 \rightleftharpoons EH_2, \\
EH_2 \rightleftharpoons EH^- + H^+, \\
EH^- \rightleftharpoons EH + \bar{e}, \\
EH^- \rightarrow EH^+ + \bar{e} \ (E = 0.03 \div 0.05\mathrm{V}), \\
EH^+ \rightleftarrows E + H^+.
\end{gathered}$$

The rate-limiting stage is the transfer of the second electron on the assumption that all the remaining stages are reversible.

Study of the possibility of direct electron transfer in electrochemical systems containing the enzyme glucose oxidase and glucose is of interest for the creation of a reagent-free glucose sensor also in biochemical fuel cells. The electrochemical oxidation of glucose at a platinum electrode with immobilised glucose oxidase has been studied.[65–68] The enzyme was fixed with the aid of glutaraldehyde or polyacrylamide gel on the surface of the electrode which had been charged beforehand or with glutaraldehyde on the uncharged electrode. The method used to modify the platinum surface has been described.[69] Positive results have been obtained only for the first method of immobilising the enzyme on the charged electrode. The steady-state currents exceed in this instance by a factor of 2–3 the currents obtained using the platinum electrode without the enzyme and reach 10 μA cm^{-2}. In the remaining cases of enzyme immobilisation on platinum catalytic effects were not observed at all. The authors explained these overall negative results by the poor contact between the enzyme and the electrode.[65] The influence of the Ag^+ and Hg^{2+} ions, which inhibit glucose oxidase, on the electrocatalytic activity of the enzyme immobilised on the surface of platinum mesh has been investigated.[70] The electrode potential established in the presence of glucose and the enzyme decreased linearly with increasing inhibitor concentration. This can serve as one of the pieces of evidence showing that in this system there is direct electron transfer between the electrode and the active centre of glucose oxidase, although other data concerning this hypothesis are not quoted.

In all the investigations enumerated above the bioelectrocatalysts were present either in a dissolved form or in an immobilised state on the surfaces of metallic and carbon electrodes. However, direct electron transfer in the enzyme–electrode system cannot be achieved in all cases using the above procedures for the immobilisation of the enzyme on the electrode.

Studies involving the use of conducting complexes of tetracyanoquinodimethane and low-molecular-weight or polymeric organic compounds as carriers for the immobilisation of enzymes are of great interest for the development of a general approach to the creation of non-mediated bioelectrocatalytic systems.[71,72] A method has been developed[73–75] for the application of polymeric electrically conducting carriers in order to achieve non-mediated electron transport in the electrode–enzyme active centre system. The inclusion of the enzyme in a current conducting matrix improves contact between the active centre of the catalyst and the carrier. Immobilisation of enzymes and the formation of matrices with a high electrical conductivity (up to 10^{-2} Ω^{-1} cm^{-1} [76]) is achieved by the coprecipitation of polymeric polycations and enzymes by means of a half-reduced tetracyanoquinodimethane (TCQDM) salt. This immobilisation procedure is also distinguished by a high capacity of the carrier with respect to the protein. The radical-ion TCQDM salts and heat-treated

polyacrylonitriles (HTPAN) have been used[73–75] to immobilise hydrogenase. Data concerning the composition, capacity with respect to the protein, electrical conductivity, and the percentage retention of enzyme activity for the polymeric carriers of hydrogenase investigated are listed in the Table. Immobilisation activates hydrogenase with simultaneous increase of the stability of the enzyme with respect to denaturation in air. It is interesting to note that one of the polymers employed, namely poly-1-propargyl-1-methyl-4,4-bipyridylium (PPMB) is a substrate of hydrogenase. The electrocatalytic properties of the hydrogenase immobilised on polymer–TCQDM complexes were investigated in relation to the formation of H_2 on a polymeric enzyme electrode, which occurs only in the presence of hydrogenase in the system. It was shown that the electron transfer to the active centre of the enzyme in the course of the study of the hydrogen formation process up to the preliminary electrochemical reduction of the carrier with hydrogenase can be achieved from any section of the polymer matrix. The poly-1-propargylpyridinium (PPP)–TCQDM polymeric conductors with immobilised glucose oxidase have been used for the electrochemical oxidation of glucose.[72] A significant increase of the current was observed only in the presence of the enzyme on the electrode and of glucose in solution. The linear dependence of the currents at a specified potential on the glucose concentration in solution was maintained in the concentration range 0.15–2.0 mM. The experimental data were described by a parabolic function and were interpreted in terms of the Michaelis–Menten equation. A linear plot obtained employing the reciprocals of the variables yielded $i_{max} = 67$ μA cm^{-2} and a Michaelis constant of $4.0 \pm 0.5 \times 10^{-3}$ M at a potential of 140 mV (Ag/AgCl).

After immobilising cytochrome b_2 on the complex of TCQDM with *N*-methylphenazine (NMP), Kulis and Svirmickas[77] observed the acceleration of the electrochemical oxidation of lactate with electron transfer from the active centre of the enzyme to the electrode without the involvement of a low-molecular-weight mediator. On the basis of this system, the same workers[78] developed a reagent-free analytical sensor for lactate.

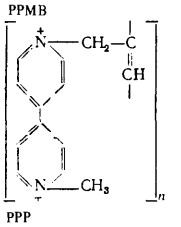
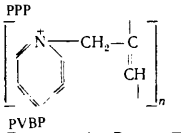
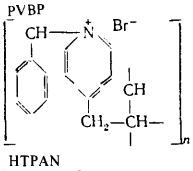
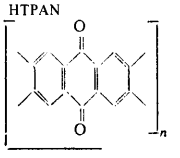
The reduction of hydrogen peroxide by peroxidase immobilised by adsorption on the NMP–TCQDM and NMA–TCQDM electrodes has been described.[79] Hydrogen peroxide was reduced at potentials of ~0.25 V relative to the saturated silver/silver chloride electrode. In the absence of peroxidase this reaction proceeds only at potentials below −0.2 V. The above studies confirm the possibility of the successful employment of radical-ion matrices ("organic metals") as electrode materials for the catalysis of electrochemical reactions by immobilised enzymes.

It is seen from the literature data quoted that there has been a growth of interest recently in the study of the direct electron transfer between the active centre of the enzyme and the electrode. However, all the studies listed above were designed to investigate the direct transfer in a specific system and were not concerned with problems of the characteristics of the electron transfer in bioelectrochemical systems as a whole

4. The Mechanism of Electron Transfer in the Enzyme Catalysis of Electrode Processes

The main problem in systems for the non-mediated oxidation or reduction of the active centre of the enzyme at the electrode involves the study of the mechanism of electron transfer from the enzyme to the electrode (or the converse process). The kinetic model of bioelectrocatalysis proposed by Varfolomeev and Berezin[80,81] cannot naturally provide an exhaustive answer. Probably the direct electron transfer requires a specific orientation of the enzyme active centre relative to the electrode and the shorter the distance from the active centre to the electrode the greater the probability of the transfer. However, the active centres of enzymes are apparently localised within the protein globule and after immobilisation can be located at an appreciable distance from the carrier surface.

Composition and characteristics of polymeric carriers.

Polymer	Probable composition of carrier	*A*, mg protein/g carrier	ρ, Ω cm	Retention of activity, %
PPMB 	$[(PPMB^{2+})(TCQDM)^{-}_{2} \cdot (TCQDM^{0}_{2})]_n$	200±20	$3.6 \cdot 10^4$	200
PPP 	$[(PPP^{+})(TCQDM)^{-}_{n}(TCQDM^{0})]_m$ $m/n = 0.25$	200±20	$1.2 \cdot 10^4$	400
PVBP 	$[(PVBP^{+})(TCQDM)^{-}(TCQDM^{0})]_n$	70±10	10^8–10^9	—
HTPAN 	HTPAN	25±5	$2.0 \cdot 10^3$	30

Notation: *A* = capacity of the carrier with respect to protein; ρ = resistivity of the carrier; PVBP = poly-1-vinyl-1-benzylpyridinium chloride.

The dependence of the efficiency of electron transfer on the distance between the active centre of laccase and the electrode has been studied[82] in relation to the electrochemical reduction of oxygen. Initially cholesterol was adsorbed on the surface of a carbon black electrode from alcoholic or heptane solutions or lecithin was adsorbed from a solution of benzene and the enzyme was then sorbed on top of the lipids. Thus the distance between the electrode and the laccase molecule increased to 6, 17, or 20 Å respectively (Fig.3). The oxygen electrochemical reduction currents at the appropriate potential were normalised with respect to the maximum rate of the enzymic reaction measured in independent experiments.

With increase of the distance from 6 to 17 Å, the authors observed a decrease of the rate of electron transfer through the cholesterol layer approximately by a factor of 4.5, while the decrease following the increase of the distance to 20 Å

(through the lecithin layer) was by a factor of ~200. The authors assume that the idea of the tunnel mechanism of electron transfer between the active centre of the enzyme and the electrode using the simple kinetic scheme

$$E + \bar{e} \rightleftharpoons E^{\neq} \xrightarrow[O_2]{} E + H_2O,$$

where E is laccase in the initial state and $E^{\neq}$ the enzyme in the reduced state, is sufficient to account for this phenomenon and also for the bioelectrocatalytic effect.

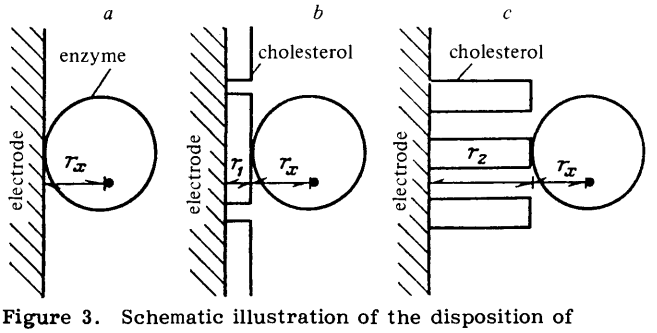


Figure 3. Schematic illustration of the disposition of the enzyme relative to the electrode surface: *a*) laccase adsorbed on the electrode surface; *b*) enzyme adsorbed on top of the liquid with a planar orientation relative to the electrode; *c*) enzyme adsorbed on top of the lipid with a vertical orientation relative to the electrode; r_1 = thickness of lipid layer with a planar orientation of cholesterol, r_2 = ditto with a vertical orientation, r_x = distance from the surface to the electron-accepting site in the enzyme.

The second stage is enzymic and limits the rate of the reaction. The first stage is electrochemical and proceeds reversibly and via the tunnel mechanism. These conclusions have been confirmed by potentiodynamic experiments under anaerobic conditions with laccase adsorbed on the electrode surface. Reversible maxima corresponding to the oxidation-reduction potential of copper of the first type, which is a primary electron acceptor in the active centre of laccase, are observed at potentials of ~+0.75 V. The tunnelling stage can be described by the equation:[83]

$$k_t(r) = A \exp(-2r/a),$$

where A is the frequency of the collisions of the electron with the potential barrier, U the height of the barrier, $a = \hbar[2m(U - E)]^{1/2}$, $\hbar$ the Planck constant, m the mass of the electron, and E the energy of the electron.

Thus in the system considered the probability of the tunnel electron transfer over a distance greater than 20 Å is sharply reduced, which has also been observed experimentally.

III. PRINCIPAL APPLICATIONS OF BIOELECTROCATALYTIC SYSTEMS

The enzymes which are effectively involved in the catalysis of electrochemical reactions can find applications in the conversion of chemical energy into electrical energy in the so-called biofuel cells.[84–86]

Using the high substrate specificity and efficiency of the catalytic action of immobilised enzymes, it appears possible to achieve the specific electrode synthesis of many organic compounds.

The application of enzymes in different kinds of electroanalytical sensors, which has been discussed by Bauman et al.[87] and by Updike and Hicks,[88] makes it possible to extend the range of compounds capable of being determined and to simplify the technique of the measurements.

1. Enzyme Electrodes

The procedure for the coupling of the enzymic and electrochemical reactions with mediation is most often used in electroanalytical enzyme sensors. The employment of these analytical devices significantly simplifies the analytical technique, makes it possible to extend the range of compounds which can be determined, and in many cases increases the sensitivity of the measurements.

The required compound, which may be electrochemically inactive, is determined from the change in the concentration of other components of the enzymic reaction (substrates or products). For example, the concentration of glucose, which is relatively inactive electrochemically, can be determined amperometrically by recording the electrochemical oxidation of the reaction product—hydrogen peroxide,[89] or the electrochemical reduction of the substrate—oxygen,[90] in reaction (1). It is also possible to follow the variation of the pH of the solution as a result of the formation of the product—gluconic acid.[91]

$$\text{Glucose} + O_2 \xrightarrow[\text{glucose oxidase}]{\text{immobilised}} \text{gluconic acid} + H_2O_2, \qquad (1)$$

$$H_2O_2 + 2I^- + 2H^+ \xrightarrow[\text{peroxidase}]{\text{immobilised}} I_2 + 2H_2O, \qquad (2)$$

$$H_2O_2 + 2\,Fe(CN)_6^{4-} + 2H^+ \xrightarrow{\text{peroxidase}} 2Fe(CN)_6^{3-} + 2H_2O. \qquad (3)$$

Another approach to the determination of glucose concentration involves the use of two-enzyme systems in which one of the products of the first enzymic reaction is the substrate of the second reaction. In this case the concentration of glucose is determined potentiometrically with the aid of an electrode sensitive to iodide ions[92] [reaction (2)] or amperometrically by recording the hexacyanoferrate(II) reduction currents [reaction (3)] at platinum or carbon electrodes.[93] A two-enzyme system employing glucose oxidase and cytochrome P-450, catalysing the conversion of aniline, by the hydrogen peroxide formed on oxidation of glucose, into *p*-aminophenol, which then undergoes anodic oxidation to the quinone, is also known. The limiting currents are then proportional to the glucose concentration.[94]

Instead of oxygen, artificial electron acceptors (AFA) may be used for the enzymic oxidation of glucose:[95]

$$\text{Glucose} + \text{oxidised AEA} \xrightarrow{\text{glucose oxidase}} \text{gluconic acid} + \text{reduced AEA}. \qquad (4)$$

Artificial electron acceptors are electrochemically active compounds and their reduced forms can be readily determined amperometrically. The possibility of determining glucose using polyviologens as AEA in the presence of oxygen has been described.[96] Measurements were made at pH 8.0, i.e. under conditions where glucose is not oxidised by oxygen in the presence of glucose oxidase. The AEA were separated from the bulk of the solution by a dialysis membrane.

Numerous methods for the determination of various organic and inorganic compounds with the aid of enzyme electrodes have now been described in the literature. These procedures as well as the construction of enzyme sensors have been discussed in detail in a number of reviews.[97-99]

Apart from being used in sensors, enzyme electrodes have been recently widely employed for medical purposes. The so-called implanted electrodes can serve as a source of energy and can transmit information about the changes in the organism. The applications and the principle of the operation of the implanted electrodes have been discussed in a review.[100]

A new type of biosensor, in which a particular effect of the enzyme reaction is converted into an electrical response by means of thermistors, transistors, or piezoelectric crystals, has appeared during the last decade.[101-103] Such analytical devices differ from those known previously by a rapid response, a high sensitivity, and universality. For example, the principle of the operation of the biothermistor is as follows. When heat is evolved as a result of an enzymic reaction, the temperature of the surrounding medium is altered and the thermistor responds to it. Over a certain range, the temperature change and hence the electrical response are proportional to the concentration of the component determined.

The new biosensors have found extensive applications in the critical analyses of a wide variety of metabolites, such as ascorbic acid, urea, glucose, creatine, cholesterol, ATP, lactate, etc., and also for the monitoring of enzymic processes. The combination of solid-phase immunoenzyme analysis with calorimetric monitoring made it possible to determine the concentrations of certain compounds below 10^{-13} M.

2. The Creation of Highly Effective Energy Converters Based on Biocatalysts

The characteristic features of enzyme catalysts make it possible to use biochemical reactions in electrochemical energy generators. There is a possibility of creating fuel cells which can use organic compounds as fuel—alcohol and carbohydrates. On the other hand, the high catalytic activity of biocatalysts makes it possible to devise fuel cells with an enhanced power, for example, in systems for the biophotolysis of water.[104]

As early as the beginning of the 1960s, the possibility of creating biochemical fuel cells was discussed.[84] Systems which can be divided into two classes exist at the present time. The first class comprises systems using biocatalysts (in the form of microorganisms, cells or enzymes) for the conversion of a particular material into an electrochemically active compound.[105-107] For example, phosphate esters and catechol and *p*-aminophenol ethers were hydrolysed[106,107] by hydrolases and the products of this reaction were then oxidised electrochemically at the electrode as the fuel. It has been shown that, when alkaline phosphatase is used, the oxidation reaction of the products of the enzymic reaction proceeds at potentials more negative by 0.3–0.4 V than the electrochemical oxidation of the initial substrates.

Methods for the conversion of complex organic substances into the simplest fuel as a result of the action of microorganisms have been described.[108-111] The primary substances employed were saccharides, urea, lactate, formic acid, and hexadecane. Ammonia, hydrogen, and methane were converted by the action of biocatalysts into a fuel capable of being oxidised at the electrode. A characteristic feature of such fuel cells is the presence of one or several stages which are not oxidation-reduction reactions and are used to convert the secondary fuel into the electrochemically active primary fuel.

The second class includes systems based on the direct utilisation of enzyme catalysts in bioelectrochemical reactions.[17] Evidently, such a function can be fulfilled only by oxidation-reduction enzymes. It is therefore promising to investigate the electrocatalytic properties of hydrogenases, glucose oxidase, acid dehydrogenases, methanol, and methane oxidases, as well as enzymes which activate the electrochemical reduction of oxygen. Fuel cells employing the enzyme glucose oxidase have been described.[66,112] The biofuel cell based on a hyaluronidase immobilised on Sepharose-CNBr reached a power output of 2.8 μW cm^{-2}.[113]

Electrodes for biofuel cells operating via a mechanism involving direct electron transfer and employing the enzymes laccase[62] and hydrogenase[114] have been described in the literature.

The so-called "cofactor-modified electrodes" can also find applications in fuel cells. The possibility of employing cofactors in electrochemical processes have been discussed in two investigations.[115,116]

A number of studies whose aim was to devise an anode for a fuel cell employing methanol as the fuel have been published in recent years.[117,118] The catalyst in this system was an NAD-independent methanol dehydrogenase and the electron acceptor was phenazine ethosulphate or phenazine methosulphate. The reduced mediator was oxidised at a platinum electrode. The cathodic reaction employed involved the reduction of oxygen on platinum. The maximum power output of the cell was 20 mW mg^{-1}.

3. Specific Electrosynthesis Under the Influence of Immobilised Enzymes

When biocatalysts are employed, it is possible to synthesise effectively compounds whose synthesis by other methods is difficult.[119,120] On the basis of the data of Wollenberger et al.,[121] it is possible to put forward a method of synthesis employing the oxidation reaction of ketosteroids catalysed by the enzyme steroid Δ^1-dehydrogenase. Wingard et al.[122] discussed the possibility of the electrosynthesis of ATP in the presence of ATP phosphatase from ADP and orthophosphate. Scheller et al.[123] proposed a method for the demethylation of benzphetamine, *p*-nitroanisole and aminopyridine in the cathodic reduction of oxygen to hydrogen peroxide in the presence of cytochrome P-450.

Methods whereby it is possible to regenerate enzyme cofactors have been recently discussed fairly frequently in the literature.[124-126] Torstensson and Johansson[127] proposed a method for the regeneration of nicotinamide-adenine dinucleotide (NAD) in a complex with alcohol dehydrogenase immobilised on the surface of a vitreous carbon electrode. The complex was obtained by employing an NAD analogue, namely $NH_2-(CH_2)_6-NHCOCH_2-NAD^+$. The electrode surface was modified with 2,4,6-trichlorotriazine. An enzymic reaction occurred in the presence of ethanol with formation of the NADH-analogue, which was then reoxidised electrochemically to the NAD-analogue. A deficiency of this method is

the occurrence of electrochemical side processes which lead to the degradation of the NAD-analogue and the formation of enzymically inactive dimeric compounds.

An NAD regenerating system employing PMS^+† as the mediator has been proposed.[128,129] The cofactor analogue NAD-dextran is reduced to NADH-dextran in the presence of substrates of the enzymes alcohol dehydrogenase and lactate dehydrogenase. NADH-dextran was oxidised chemically in the presence of PMS^+ to NAD-dextran. The PMSH formed is oxidised reversibly to PMS^+ at the electrode. The proposed method also makes it possible to regenerate NADP in the presence of glutamate dehydrogenase. The efficiency of the regeneration of the cofactor in such systems reaches 99.85%.

Reactions involving the electrosynthesis of a number of carbohydrate derivatives using methane monoxygenase have been described.[48,119]

It is to be expected that interest in the preparation of organic substances of this kind with the aid of the bioelectrosynthetic method will steadily grow. This is associated with the necessity for the large-scale manufacture of certain substances, for example, for the pharmaceutical industry, whose synthesis by the known organic synthetic methods is difficult.

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† PMS^+ and PMSH are the oxidised and reduced forms of phenazine methosulphate respectively (Ed.of Translation).

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The Reactivity of Polyfunctional Compounds in Radical Reactions

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Recent results of studies of the kinetics of the reactions of monohydric and polyhydric alcohols and polyfunctional esters with peroxy- and alkyl radicals, oxygen, and hydroperoxide are examined. By comparing the reactivities of mono- and polyfunctional compounds in relation to polar reagents, it is shown that the rule of the additivity of the partial rate constants breaks down in all cases. The data are analysed within the framework of the concept of the multidipolar interaction of the polar groups in the molecule and the transition state and the complete agreement between the published results and the conclusions based on this concept is demonstrated.
The bibliography includes 31 references.

CONTENTS

I. Introduction 863
II. The structural factors which determine the reactivity of molecules 863
III. The reactions of peroxy-radicals with polyhydric alcohols and polyfunctional esters 865
IV. The reactions of polyfunctional esters with hydroperoxide and oxygen 868
V. The multidipolar model of the transition state for the reaction of a polar species with a polyfunctional molecule 869
VI. Analysis of experimental data within the framework of the concept of the multidipolar interaction in the transition state 871

I. INTRODUCTION

The reactivity of molecules in radical reactions depends both on their structure and on the structure of the attacking radical. The following factors influence the reactivity of molecules in radical abstraction and addition reactions. The first factor is the heat of reaction: the higher the heat, the faster the reaction; the dependence of the activation energy on the heat of reaction within the limits of a single reaction series can be fitted by the Polanyi–Semenov equation.[1] The second factor is the polarity (polar structure) of the transition state: the shift of electron density in the transition state from one atom to another lowers the activation energy.[2] The third is the steric factor associated with the presence of bulky substituents adjoining the reaction centre which hinder the attack by the radical.[2] All three factors depend on the nature of the atoms participating in the reaction and on the structure of the substituents. The molecule of an organic compound can therefore be subjected to an imaginary sub-division into a series of fragments and the reaction rate constant can be represented by the sum of the partial rate constants referred to the corresponding fragments. This additivity rule for radical reactions frequently holds satisfactorily and is fairly widely used.[3]

Comparison of the rate constants for the reactions of peroxy-radicals with monocarboxylic and dicarboxylic acid esters[4] and also for the reaction of the cumenylperoxy-radicals with diethylene glycol dicaprylate and pentaerythritol tetravalerate[5] revealed the failure of this rule. These facts served as the starting point for the development of the concept of the dipole–dipole interaction between the polar agent and the dipole moments of the polar groups in the polyfunctional molecule,[6] which has been referred to as multidipolar interaction, since several (more than two) dipolar groups are involved in it. Evidence concerning the validity of the above concepts has been obtained very recently for a wide variety of radical reactions. This review is devoted to the analysis and survey of these data.

II. THE STRUCTURAL FACTORS WHICH DETERMINE THE REACTIVITY OF MOLECULES

The rate constant for the elementary reaction of a radical with a molecule depends on the heat of reaction (the Polanyi–Semenov rule), the polarity of the transition state, the accessibility of the reaction centre, and the temperature and nature of the medium. The reactivity of the molecule is influenced by bond conjugation, by the inductive effect, and by the steric factor.

Each of the three factors indicated can influence the heat of reaction. The scale of this influence can be inferred by comparing the C–H bond strengths in the corresponding compounds. For example, the contribution of the conjugation effect can be estimated by comparing the C–H bond strengths in the methane (435 kJ mol^{-1}) and toluene (355 kJ mol^{-1}) molecules.[7] The difference of 80 kJ mol^{-1} is caused in this case by the fact that the free valence in the benzyl radical is conjugated with the π orbitals of the benzene ring. The decrease of the C–H bond dissociation energy from 435 kJ mol^{-1} in methane to 410 kJ mol^{-1} in methyl bromide is associated with the polar effect exerted by the bromine atom.[7] In ethanol the energy of the α-C–H bond is lower by 34 kJ mol^{-1} than in ethane, where D_{C-H} = 410 kJ mol^{-1} [7] owing to the combined influence of the inductive effect (the shift of the σ electrons along the C–O bond) and the effect of the conjugation of the free valence with the pair of p electrons of oxygen. Comparison of ethylbenzene and indan may serve as an example of the influence of the steric effect on the C–H bond strength. The methyl group in the α-phenylethyl radical prevents the most complete overlap of the p orbital of the unpaired electron with the π orbitals of the benzene ring. The α-C–H bond in ethylbenzene is therefore somewhat stronger than in indan and the phenyl radical attacks the indan α-C–H bond four times faster than that in ethylbenzene.[8]

The polar factor, which is manifested when the radical (atom) and the molecule have different electron affinities, is also very important.[8] An example may be provided by a

comparison of the reactions of chlorine and hydrogen with methane. Since the H–H and H–Cl bond strengths are equal (426 kJ mol^{-1}), it follows that the heats of these two reactions are also equal (−8 kJ mol^{-1}). Nevertheless the activation energies for these reactions differ by 38 kJ mol^{-1}: E = 54 kJ mol^{-1} for the reaction of hydrogen with methane and E = 16 kJ mol^{-1} for the reaction of chlorine with methane.[9] Such a marked decrease of activation energy on passing from H to Cl has been accounted for by the polar structure of the transition state Cl...H...CH_3 in which the Coulombic attraction in the fragments bearing unlike charges reduces the potential barrier. The polar structure of the transition state is determined in its turn by the high electron affinity of the chlorine atom (346 kJ mol^{-1}).

The inductive effect influences both the heat of reaction and the polar character of the transition state. For example, in the reactions of bromine atoms with the C–H bonds of cyclohexane and toluene the principal factor is the heat of reaction. The C–H bond in toluene (D_{R-H} = 355 kJ mol^{-1}) is much weaker than in cyclohexane (D_{R-H} = 393 kJ mol^{-1}) [7] and toluene is accordingly brominated 17 times faster than cyclohexane (at 353 K).[8] On the other hand, chlorine atoms attack cyclohexane molecules four times faster than toluene molecules (at 313 K).[8] This "inversion" of the reactivities of the molecules can be accounted for by the different contributions of the heat of reaction and the polar factor to the activation energy for the reaction. The reaction of bromine with toluene is thermally neutral, while that with cyclohexane is endothermic (q = 38 kJ mol^{-1}) and the relative reactivities of toluene and cyclohexane are therefore determined by the strengths of their C–H bonds. while the polar structure is of secondary importance.

The reaction of chlorine (D_{H-Cl} = 426 kJ mol^{-1}) is extremely exothermic with both toluene (q = 71 kJ mol^{-1}) and cyclohexane (q = 33 kJ mol^{-1}).[7] The polar effect, which is greater in the case of cyclohexane, therefore makes a decisive contribution to the decrease of activation energy.

Another example involves the attack by various species on the C–H bonds in the propionic acid molecule.[8] The methyl radical attacks predominantly the α-CH_2 group (at 373 K the α-C–H bond is attacked 8 times faster than the β–C–H bond). On the other hand, the chlorine atom attacks the stronger β–C–H bond 33 times faster than the weaker α–C–H bond (at 353 K). The ratio of the rate constants for the methyl radical is determined by the strengths of these bonds. On the other hand, the chlorine atom attacks faster in those cases where a more polar transition state is produced; this is hindered by the presence of the electron-accepting carboxy-group in the α-position. A relation between the rate constant, on the one hand, and the ionisation potential of the molecule I(RH) and the electron affinity of the peroxy-radical EA($RO_2^{\cdot}$), on the other, has been found empirically for the reactions of peroxy-radicals with aromatic alkyl-substituted hydrocarbons;[10] at 348 K the relation is of the form $\Delta \lg k = 31.48\ [I(RH) - EA(RO_2^{\cdot})]^{-1}$.

Finally, the third factor determining the reactivity is the accessibility of the reaction centre, which depends on the size and number of the bulky substituents near the reaction centre and on the conformation of the molecule. For example, the phenyl radical abstracts an H atom from hydrocarbons having the structure $(CH_3)_3C(CH_2)_nCH(CH_3)_2$ with relative rate constants of 0.71 (n = 0), 0.34 (n = 1), and 0.81 (n = 2),[8] i.e., instead of a smooth increase of the rate constant with increasing n, its decrease (by a factor of two) on passing from n = 0 to n = 1, i.e. after the appearance of one CH_2 group, is observed. An analogous relation (a periodic relation as a function of the number of CH_2 groups) has been observed for the reactions of the undecyl radical with the esters $CH_3OCO(CH_2)_nCOOCH_3$.[11]

All three effects (the inductive effect, the conjugation effect, and the steric effect) are local in character. The inductive effect is transmitted via the σ-bonds and rapidly decays: at the third carbon atom starting from the atom attached to a polar substituent it is no longer manifested. For the manifestation of an appreciable influence of the conjugation effect, a double bond or an aromatic ring must adjoin this atom (i.e. must be located in the 2-position). The steric effect is also manifested only in the vicinity (in the α-position and more weakly in the β-position) of the bulky substituent. The molecule whose C–H bonds are attacked by free radicals can therefore be subdivided into a series of structural groups, each of which enters into the reaction with its own partial rate constant. The rule of the additivity of the partial rate constants follows from this approach: the rate constant for the reaction of a free radical with a molecule is equal to the sum of the partial rate constants k_i for all the fragments constituting the molecule, i.e.

$$k = \sum_i^n k_i.$$

The rule of additivity holds fairly well in many cases. For example, it has been clearly established that, in the reactions of free radicals with hydrocarbons,[3] aliphatic acids, and esters, the reaction rate constant increases linearly with the number of methylene groups.[4] Table 1 presents the partial rate constants for the reactions involving the abstraction of a hydrogen atom by the $CH_3^{\cdot}$, $RO^{\cdot}$, and $RO_2^{\cdot}$ radicals.

Table 1. The partial rate constants (k, litre mol^{-1} s^{-1}) for the abstraction of H atoms from the C–H bonds in various groups.

Group	$CH_3^{\cdot}$ (338 K) [3]	$(CH_3)_3OO^{\cdot}$ (313 K) [3]	$(CH_3)_3COO^{\cdot}$ (303 K) [12]
$-CH_3$	5.0	$2.5\cdot10^4$	—
$>CH_2$	50	$1.4\cdot10^5$	$2.7\cdot10^{-4}$
$>CH$	500	$3.8\cdot10^5$	$4.8\cdot10^{-3}$
$>C{=}CHCH_3$	18	$4.8\cdot10^5$	—
$>C{=}CHCH_2{-}R$	120	$1.4\cdot10^4$	$8.4\cdot10^{-2}$
$C_6H_5{-}CH_3$	420	$2.4\cdot10^5$	$1.2\cdot10^{-2}$
$C_6H_5{-}CH_2R$	560	$1.6\cdot10^5$	0.10
$C_6H_5CH(CH_3)_2$	$1.8\cdot10^3$	$8.4\cdot10^4$	0.16
$>CHOH$	$3.4\cdot10^3$	—	$9\cdot10^{-3}$
$-CO-CH_2-$	850	$8.5\cdot10^4$	—

Note. The numerals in square brackets denote references (Ed. of Translation).

The rule of additivity is well known from experiments involving the reactions of atoms (H, Cl, Br) and free radicals ($HO^{\cdot}$, $RO_2^{\cdot}$, $CH_3^{\cdot}$, $CF_3^{\cdot}$) with hydrocarbons and monofunctional organic compounds.[3] The rule also holds for reactions of peroxy-radicals with hydrocarbons. Even in the oxidation of dicarboxylic acids and their esters, it holds in relation to the methylene groups in the molecule.[4] For example, the rate constants for the reaction of cumenylperoxy-radicals with the dimethyl esters of dicarboxylic acids increase linearly with increase in the number n of methylene groups in the acid residue: $\log k = 9.6 + 0.73n$ litre $mole^{-1}$ s^{-1} at

413 K. The situation is exactly the same for the dependence of k on the number of CH_2 groups in the alcoholic residue when the cumenylperoxy-radical attacks the molecule of a dibasic acid ester and the alcohol residue in the molecule is varied.[4] However, as shown below, in many reaction series the rule of the additivity of the partial rate constants does not hold, i.e. for a molecule consisting of n fragments we have

$$k \neq \sum_i^n k_i,$$

where k_i refers to the ith fragment. The deviation from the additivity rule can be characterised, for example, by the ratio

$$\sum k_i/k$$

or its logarithm. Using the theory of the absolute reaction rates, the deviation can be characterised in terms of the change in the Gibbs free energy of activation as

$$\Delta\Delta G_{ad}^{\neq} = \Delta G^{\neq} - \Delta G_{ad}^{\neq} = RT \ln \left(\sum_i k_i/k \right),$$

where $\Delta G_{ad}^{\neq}$ is the Gibbs activation energy for the molecule when the rule of additivity holds.

III. THE REACTIONS OF PEROXY-RADICALS WITH POLYHYDRIC ALCOHOLS AND POLYFUNCTIONAL ESTERS

Valuable experimental data on the reactivities of polyfunctional esters in reactions with cumenylperoxy-radicals have been obtained in the study of the oxidation of the esters in the presence of cumenyl hydroperoxide, which serves simultaneously also as the initiator of the reaction and as the source of cumenylperoxy-radicals.[11,13] The experimental conditions ensured in the system an intense exchange of the $RO_2^{\cdot}$ radicals for cumenylperoxy-radicals. The chain oxidation scheme in a system of this kind includes the following reactions:

$$\mathrm{ROOR} \xrightarrow{k_i} 2\mathrm{RO}^{\cdot} \xrightarrow{\mathrm{R'H}} \dot{\mathrm{R}}';$$

$$\mathrm{ROOH} \xrightarrow{k_{i,\mathrm{ROOH}}} \mathrm{RO}^{\cdot} + {}^{\cdot}\mathrm{OH} \xrightarrow{\mathrm{R'H}} \dot{\mathrm{R}}';$$

$$\dot{\mathrm{R}}' + \mathrm{O}_2 \rightarrow \mathrm{R'OO}^{\cdot};$$

$$\mathrm{R'OO}^{\cdot} + \mathrm{ROOH} \rightleftharpoons \mathrm{R'OOH} + \mathrm{RO}_2^{\cdot};$$

$$\mathrm{R'OO}^{\cdot} + \mathrm{R'H} \xrightarrow{k_p'} \mathrm{R'OOH} + \dot{\mathrm{R}}';$$

$$\mathrm{RO}_2^{\cdot} + \mathrm{R'H} \xrightarrow{k_p} \mathrm{ROOH} + \dot{\mathrm{R}}';$$

$$\mathrm{RO}_2^{\cdot} + \mathrm{RO}_2^{\cdot} \xrightarrow{k_t} \mathrm{ROOR} + \mathrm{O}_2;$$

$$\mathrm{R'O}_2^{\cdot} + \mathrm{RO}_2^{\cdot} \xrightarrow{k_t'} \mathrm{R''{=}O} + \mathrm{O}_2 + \mathrm{ROH};$$

$$\mathrm{R'O}_2^{\cdot} + \mathrm{R'O}_2^{\cdot} \xrightarrow{k_t''} \mathrm{R''{=}O} + \mathrm{O}_2 + \mathrm{R'OH}.$$

For sufficiently long chains and when the reaction of $\dot{\mathrm{R}}'$ with O_2 is very rapid, the rate of chain oxidation is described by the expression $v_{\mathrm{O}} = \{k_p[\mathrm{RO}_2^{\cdot}] + k_p'[\mathrm{R'O}_2^{\cdot}]\}[\mathrm{RH}] = a[\mathrm{RH}]v_i^{1/2}$; the variation of the ratio [ROOH]/[R'H] entails the variation of the coefficient a, which depends on the composition of the radicals, i.e. on the ratio $[\mathrm{RO}_2^{\cdot}]/[\mathrm{R'O}_2^{\cdot}]$. When [ROOH] = 0, the coefficient $a = k_p'(2k_t'')^{-1/2}$, and when [ROOH] $\rightarrow \infty$, we obtain $a \rightarrow k_p(2k_t)^{-1/2}$. The experiments were performed for [ROOH] $\geqslant$ 0.8 M,[13] whereupon the coefficient a reaches its maximum value of 6×10^{-3} litre$^{1/2}$ mol$^{-1/2}$ s$^{-1/2}$. The results of the measurement of $k_p(2k_t)^{-1/2}$ are presented in Table 2. The absolute values of k_p were calculated on the assumption that $2k_t = 4.05 \times 10^6$ litre mol^{-1} s^{-1} for cumenyl peroxide.[15]

With increase of the number of ester groups in the molecule, the partial rate constant k_{pi} also increases. If it is assumed, after Pozdeeva et al.,[14] that $\Delta \lg k_{pt} = \delta n$, where n is the number of ester groups, then we obtain $k_{pi} = 1.0$ litre mol^{-1} s^{-1} for the monoester ($n = 1$). This makes it possible to calculate $\Delta\Delta G_{ad}^{\neq}$, which varies in the series of propionate esters from 0 to −4 kJ mol^{-1}. In this series of compounds, the increase of the number of functional groups in the molecule increases the reactivity of the C−H bonds in each group. Another tendency has been observed for esters obtained from different aliphatic acids. Only the $-OCH_2-$ groups are apparently attacked in pentaerythritol tetraacetate, so that $k_{CH_2O} = 0.25\, k_p = 2.0$ litre mol^{-1} s^{-1}. For the attack by the cumenylperoxyradical on the α-CH_2 group of the acid residue in pentaerythritol tetrapropionate, we obtain $k_{\alpha\text{-}CH_2} = 0.25k_p - 2.0 = 1.5$ litre mol^{-1} s^{-1}. For pentaerythritol tetracaprate, the average value of k_{CH_2} for the methylene groups in the acid residue is significantly higher: $k_{CH_2} = (87.7 - 8.1)/32 = 2.5$ litre mol^{-1} s^{-1}. In the n-heptadecane molecule (see Table 3 below) the methylene group reacts with $RO_2^{\cdot}$, for which $k_{CH_2} = 2.8$ litre mol^{-1} s^{-1}.

Table 2. Kinetic parameters of the oxidation reaction of esters in the presence of cumenyl hydroperoxide (404 K, *o*-dichlorobenzene).[13,14]

Ester	$k_p'(2k_t'')^{-1/2} \times 10^3$, litre$^{1/2}mol^{-1/2}s^{-1/2}$	k_p, litre mol^{-1}s^{-1}	k_p^0, litre mol^{-1}s^{-1}*	$\Delta\Delta G_{ad}^{\neq}$, kJ mol^{-1}
$C(CH_2OCOCH_3)_4$	2.82	8.1	2.0	—
$C(CH_2OCOCH_2CH_3)_4$	3.69	13.9	3.5	−4.1
$CH_3CH_2C(CH_2OCOCH_2CH_3)_3$	2.62	6.4	2.1	−2.5
$(CH_3)C(CH_2OCOCH_2CH_3)_2$	1.27	3.0	1.5	−1.4
$CH_3CH_2OCOC(CH_2)_3CH_3$	2.26	5.0	5.0	—
$C[CH_2OCO(CH_2)_6CH_3]_4$	26.2	87.7	22	—
$[CH_2OCO(CH_2)_6CH_3]_2$	8.65	28.5	—	—
$[CH_2OCH_2CH_2OCO(CH_2)_6CH_3]_2$	15.84	54.7	—	—
n-$C_{17}H_{36}$	12.50	41.7	2.8	—

*Here k_p^0 represents the constant recalculated for one fragment.

Evidently the ester group lowers the reactivity of the nearest methylene groups of the acid residue and, on moving away from the OCO group, the reactivity of the methylene groups increases, tending to that in an n-paraffin molecule.

The coupled oxidation of a number of ethers and esters with n-decane has been studied.[16] The ratio of the rate constants for the reactions of decylperoxy-radical with the ester or ether and n-decane has been estimated from the dependence of the rate of the initiated oxidation on the concentration of the ester or ether added to the hydrocarbon. The relative partial rate constants (at 403 K) were obtained from a comparison of the relative rates with the structures of the monofunctional esters and ethers: 0.125 for the CH_2 group, 2.4 for the OCH_2 group, and 0.4 for the CH_2OCO. $.(CH_2)_6$ group. Calculation assuming additivity for diethylene glycol dicaprylate yielded $k_{rel} = 5.2$, while the experimental value is 2.8. $\Delta\Delta G_{ad}^{\neq} = 2.1$ kJ mol^{-1} corresponds to this deviation from additivity.

Apart from ethers and esters, the reactivity of polyhydric alcohols in reactions with peroxy-radicals has been investigated.[16,17] This reaction has been studied[17] by the method of coupled oxidation with a selective inhibitor,[18] in which the ability of peroxy-radicals derived from the alcohol to reduce certain compounds, particularly quinones, was used.[19] Under the conditions of the coupled chain oxidation, such a selective inhibitor lowers the rate of the process to an extent which depends on the rate of generation of the hydroxyperoxy-radicals from the alcohol: the faster the formation of these radicals, the more pronounced the inhibiting effect of the inhibitor. This makes it possible to determine the reactivity of the alcohol in relation to $RO_2^{\cdot}$ compared with the reactivity of RH. In the presence of a selective inhibitor Q (quinone) and an initiator I, the coupled oxidation of an alcohol HR'OH and the substance RH includes the following stages:[18]

$$I \xrightarrow{v_i} \dot{r} \xrightarrow{RH} \dot{R} \xrightarrow{O_2} RO_2^{\cdot};$$

$$RO_2^{\cdot} + RH \xrightarrow{k_p} ROOH + \dot{R};$$

$$RO_2^{\cdot} + HR'OH \xrightarrow{k_p'} ROOH + \dot{R}'OH;$$

$$O_2 + \dot{R}'OH \xrightarrow{fast} \dot{O}OR'OH;$$

$$\dot{O}OR'OH + Q \rightarrow \dot{Q}H + O_2 + R'{=}O;$$

$$RO_2^{\cdot} + \dot{Q}H \xrightarrow{fast} ROOH + Q;$$

$$RO_2^{\cdot} + RO_2^{\cdot} \xrightarrow{k_t} \text{products}.$$

At a sufficiently high concentration of Q in the system, the $RO_2^{\cdot} + RO_2^{\cdot}$ reaction does not play any role in chain termination and the peroxy-radicals derived from the alcohol react with Q so fast that the rate of reaction is limited by their formation via the reaction of $RO_2^{\cdot}$ with the alcohol.

Under these conditions, the rate of the inhibited oxidation is defined by the expression

$$v = k_p[RH][RO_2^{\cdot}] + v_i \cong k_p[RH][RO_2^{\cdot}],$$

where

$$v_i = 2k_p'[HR'OH][RO_2^{\cdot}],$$

and the rate constant ratio k_p'/k_p is found from the equation $k_p'/k_p = v_i[RH]/2v[HR'OH]$. Degtyareva et al.[16] carried out experiments under conditions such that the chains are short (the chain length was $\nu < 10$) and the degree of inhibition was low ($\nu/\nu_0 > 0.3$). Under these conditions, it is not permissible to neglect either v_i or the contribution by the $RO_2^{\cdot} + RO_2^{\cdot}$ reaction, i.e. it is necessary to take into account the fact that the following equalities hold in the quasi-stationary regime in the presence of Q: $k_p[RH][RO_2^{\cdot}] = v - v_i$ and $v_i = 2k_p'[HR'OH][RO_2^{\cdot}] + 2k_t[RO_2^{\cdot}]^2$. Bearing in mind that $v = v_0 = k_p(2k_t)^{-1/2}[RH]v_i^{1/2}$ when [Q] = 0, we arrive at the following formula after simple rearrangements:

$$\frac{k_p'}{k_p} = \frac{1}{2}\frac{[RH]}{[HR'OH]}\left\{\frac{1}{\nu - 1} - \frac{\nu - 1}{\nu_0^2}\right\},$$

where $\nu = v/v_i$ and $\nu_0 = v_0/v_i$. This formula is more accurate than that quoted in Ref.17 and was used to recalculate the k_p'/k_p ratios from the experimental data of the earlier study.[17] The results of the calculation are presented in Table 3.

$\Delta\Delta G_{ad}^{\neq}$ can be estimated more conveniently for the absolute values of k_p'. Following the procedure of Degtyareva et al.,[16] we assume that k_p is the same as for the reaction of cumenylperoxy-radicals with n-hexadecane. According to Denisov et al.,[4] $k_{pi} = 0.31$ litre mol^{-1} s^{-1} at 403 K for the reaction of the cumenylperoxy-radical with one methylene group of an n-paraffin, so that we obtain $k_p = 14 \times 0.31 = 4.3$ litre mol^{-1} s^{-1} for the reaction of $RO_2^{\cdot}$ with n-hexadecane (neglecting the attack by the peroxy-radicals on the methyl groups). On the basis of data for the coupled oxidation of n-hexadecane together with 1-decanol and 2-octanol[17] and assuming that the methylene groups in the alcohol molecules are attacked with the same partial rate constant as in the n-paraffin molecule, we obtain the following partial rate constants: $k_{CH_2OH} = 34.8 - 8 \times 0.31 = 32.3$ litre mol^{-1} s^{-1} and $k_{CHOH} = 43.4 - 5 \times 0.31 = 41.9$ litre mol^{-1} s^{-1}. Proceeding in exactly the same way as for the diethylene glycol dicaprylate–alcohol system and assuming that $k_p = 4.6$ litre mol^{-1} s^{-1},[5] we obtain $k_{CH_2OH} = 22.5 - 2.5 = 20$ litre mol^{-1} s^{-1} for 1-decanol and $k_{CH_2OH} = 23.0 - 2.2 = 20.8$ litre mol^{-1} s^{-1} for 1-nonanol; these values are very close and one can adopt the average $k_{CH_2OH} = 20.4$ litre mol^{-1} s^{-1}. On the basis of the data for 2-octanol (Table 3), we obtain $k_{CHOH} = 22.5 - 1.5 = 21$ litre mol^{-1} s^{-1}. Table 4 presents the values of k_p', the constants k_Σ obtained assuming additivity, and the values of $\Delta\Delta G_{ad}^{\neq}$ calculated on this basis. It is seen that polyhydric alcohols do not obey the rule of additivity in reactions with peroxy-radicals.

Table 3. The results of the measurement of k_p'/k_p for a number of alcohols by the method of coupled oxidation in the presence of a selective inhibitor {404 K, [Q] = 10^{-2} M, initiator—di-t-butyl peroxide}.[17]

Alcohol	k_p'/k_p	
	1	2
$CH_3(CH_2)_8CH_2OH$	8.1±0.6	4.9±0.8
$CH_3(CH_2)_7CH_2OH$	—	5.0±0.4
$CH_3CHOH(CH_2)_5CH_3$	10.1±1.4	4 9±0.7
$HOCH_2CH_2OH$	3.5±0.6	—
$HOCH_2CH_2CH_2CH_2OH$	3.9±0.2	3.1±0.1
$HOCH_2CH_2CHOHCH_3$	5.2±0.2	3.4±0.3
$HOCH_2C(CH_3)_2CH_2OH$	154±37	26.3±2.1
$CH_3CH_2C(CH_2OH)_3$	42±6	25.7±4.8
$[HOCH_2CH(OH)CH_2]_2O$	70±9	15.4±0.6
$CH_3CHOHCHOHCH_3$	—	5.8±1.2

Notation: 1) results obtained in experiments with hexadecane ($v_i = 1.3 \times 10^{-6}$, $v_0 = 7.6 \times 10^{-6}$ mol litre^{-1} s^{-1}); 2) results obtained in experiments with diethylene glycol dicaprylate ($v_i = 8.3 \times 10^{-7}$, $v_0 = 8.0 \times 10^{-6}$ mol litre^{-1} s^{-1}).

The coupled oxidation of a number of monohydric and polyhydric alcohols together with n-decane, n-hexadecane, and polyfunctional esters has been investigated.[16] Experimental measurements were made of the dependence of the rate of the initiated chain oxidation on the composition of the binary mixture (at 403 K using di-t-butyl peroxide as the initiator). The following scheme comprising reactions limiting the rate of chain propagation and termination is valid for the initiated chain oxidation (RH is a hydrocarbon or ester and HR'OH is an alcohol):

$$RO_2^{\cdot} + RH \xrightarrow{k_{p,11}} ROOH + R^{\cdot};$$

$$RO_2^{\cdot} + HR'OH \xrightarrow{k_{p,21}} ROOH + \dot{R}'OH;$$

$$HOR'O_2^{\cdot} + RH \xrightarrow{k_{p,12}} HOR'OOH + R^{\cdot};$$

$$HOR'O_2^{\cdot} + HR'OH \xrightarrow{k_{p,22}} HOR'OOH + \dot{R}'OH;$$

$$\left.\begin{aligned} RO_2^{\cdot} + RO_2^{\cdot} &\xrightarrow{k_{t,11}} \\ RO_2^{\cdot} + HOR'OO^{\cdot} &\xrightarrow{k_{t,12}} \\ HOR'O_2^{\cdot} + HOR'OO^{\cdot} &\xrightarrow{k_{t,22}} \end{aligned}\right\} \text{molecular products.}$$

The rate of the coupled chain oxidation with v_i = const is described by the expression

$$v = \frac{(k_{p,11} + k_{p,12}u)\cdot[RH] + (k_{p,21} + k_{p,22}u)\cdot[HR'OH]}{(2k_{t,11} + 2k_{t,12}u + 2k_{t,22}u^2)^{1/2}} \cdot v_i^{1/2},$$

where

$$u = k_{p,21}[HR'OH]/k_{p,12}[RH].$$

For low amounts of added alcohols, where the contribution of the $HOR'OO^{\cdot}$ + HR'OH reaction to chain propagation and the contribution of the $HOR'OO^{\cdot}$ + $HOR'OO^{\cdot}$ reaction to chain termination may be neglected, the expression for the rate of the coupled oxidation assumes a simpler form:

$$\frac{v}{v_0} = \left(1 + 2\frac{k_{p,21}[HR'OH]}{k_{p,11}[RH]}\right)\cdot\left(1 + \frac{k_{t,12}}{k_{t,11}}\cdot\frac{k_{p,21}}{k_{p,12}}\cdot\frac{[HR'OH]}{[RH]}\right)^{-1/2},$$

whence the following relation can be obtained:

$$\alpha = \frac{\Delta v}{v_0}\Big/\Delta\left(\frac{[HR'OH]}{[RH]}\right) = 2\frac{k_{p,21}}{k_{p,11}} - \frac{1}{2}\frac{k_{t,12}}{k_{t,11}}\cdot\frac{k_{p,21}}{k_{p,12}},$$

where $\Delta v = v - v_0$ and $v_0 = k_p(2k_{t,11})^{-1/2}[RH]v_i^{1/2}$ is the rate of oxidation of RH in the absence of HR'OH under the same conditions. The coefficient α is determined from the experimental dependence of v on [HR'OH]/[RH].

Table 4. Deviation from additivity in the reactions of peroxy-radicals with polyhydric alcohols (403 K)*.

Alcohol (group)	k'_p/k_p	k'_p, litre mol^{-1}s^{-1}	k_Σ, litre mol^{-1}s^{-1}	$\Delta\Delta G^{\neq}_{ad}$, kJ mol^{-1}
n-Hexadecane, k_p = 4.3 litre mol^{-1}s^{-1}				
$-CH_2OH$	—	32.3	—	—
>CHOH	—	41.9	—	—
$HOCH_2CH_2OH$	3.5	15	64.6	4.9
$(CH_2CH_2OH)_2$	3.9	16.8	65.2	4.9
$HOCH_2CH_2CH(OH)CH_3$	5.2	22.4	74.5	4.0
$(CH_3)_2C(CH_2OH)_2$	154	662	64.6	—7.8
$CH_3CH_2C(CH_2OH)_3$	42	181	97.2	—2.1
Diethylene glycol dicaprylate, k_p = 4.6 litre mol^{-1}s^{-1}				
$-CH_2OH$	—	20.4	—	—
>CHOH	—	21.0	—	—
$-OCH_2-$	—	90	—	—
$(CH_2CH_2OH)_2$	3.1	14.3	41.4	3.6
$HOCH_2CH_2CH(OH)CH_3$	3.4	15.6	41.7	3.3
$CH_3CH(OH)CH(OH)CH_3$	5.8	26.7	42.0	1.5
$(HOCH_2)_2C(CH_3)_2$	26.3	121	40.8	—3.7
$CH_3CH_2C(CH_2OH)_3$	25.7	118	61.5	—2.2

*The ratios k'_p/k_p were taken from Table 3.

The rate constant ratio $k_{p,21}/k_{p,11}$ in which we are interested can be obtained from α by estimating the second term in the above formula, which can be done in the following manner. It is known that the reactivity of the peroxy-radical depends only slightly on its structure and one can put $k_{p,12} = k_{p,11}$. In this case the expression for the parameter α becomes

$$\alpha = 2(k_{p,21}/k_{p,11})\cdot(1 - 0.25\ k_{t,12}/k_{t,11}).$$

The ratio $k_{t,12}/k_{t,11}$ may be estimated by comparing the values of α and $k_{p,21}/k_{p,11}$ measured by the method of coupled oxidation with the selective inhibitor described above. Table 5 presents such a comparison; it is seen that always the ratio $k_{t,12}/k_{t,11} > 1$ and the average value is 2.5 ± 0.6. We obtain the formula

$$k_{p,21}/k_{p,11} = 1.33\alpha.$$

for the calculation of $k_{p,21}/k_{p,11}$. We recalculated the values of $k_{p,21}/k_{p,11}$ from the data of Degtyareva et al.[16] in terms of this formula and the results are presented in Table 6.

In order to calculate the partial rate constants, we proceed in the following way. For the alcohol–hexadecane system, where all the methylene groups in RH are equivalent as regards their reactivity, we have $k_{p,11} = 14k_{CH_2}$ and $k_{p,21}/k_{p,11} = 14k_{p,21}/k_{CH_2}$. In the n-decane molecule the peroxy-radical attacks 8 methylene groups and the CH_2OH group; consequently

$$k_{p,21}/k_{CH_2} = 74.2 = k_{CH_2OH}/k_{CH_2} + 8,$$

whence

$$k_{CH_2OH}/k_{CH_2} = 66.2.$$

Analogously, on the basis of the ratio $k_{p,21}/k_{CH_2}$ for 2-octanol, we obtain $k_{CHOH}/k_{CH_2} = 156$. Using the rule of additivity, we obtain $k_{p,21}/k_{CH_2}$ for butane-1,3-diol and for 1,1,1-tri(hydroxymethyl)propane (Table 6).

Table 5. Comparison of the values of α and $k_{p,21}/k_{p,11}$ for coupled chain oxidation of alcohols together with n-hexadecane (403 K).

Alcohol	α [13]	$k_{p,21}/k_{p,11}$ [16]	$k_{t,12}/k_{t,11}$
$CH_3(CH_2)_8CH_2OH$	4.0	8.1	3.0
$CH_3CH(OH)(CH_2)_5CH_3$	8.4	10.1	1.7
$CH_3CH_2C(CH_2OH)_3$	18	42	3.1
$CH_2CH(OH)CH_2CH_2OH$	5.4	5.2	2.1

Note. The numbers in square brackets denote references (Ed. of Translation).

Table 6. The results of the study of the coupled oxidation of alcohols together with n-hexadecane and esters (403 K, initiator—di-t-butyl peroxide).[16]

RH	HR'OH(R'H)	α	$k_{p,21}/k_{p,11}$	$k_{p,21}/k_{CH_2}$	$k_{p,21}/k_{CH_2}$ (calc.)	$\Delta\Delta G^{\neq}_{ad}$, kJ mol^{-1}
$CH_3(CH_2)_{14}CH_3$	$CH_3(CH_2)_8CH_2OH$	4.0	5.3	74.2	742	—
»	$CH_3CH(OH)(CH_2)_5CH_3$	8.4	11.2	161	161	—
»	$HOCH_2CH_2CH(OH)CH_3$	5.4	7.2	101	223	2.6
»	$CH_3CH_2C(CH_2OH)_3$	17.7	23.5	329	119.6	—1.7
$[CH_2OCH_2CH_2OCO(CH_2)_6CH_3]_2$	$CH_3(CH_2)_8CH_3$	0.17	0.2	0.025	0.025	—
»	$CH_3(CH_2)_8CH_2OH$	1.6	2.1	84	84	—
»	$CH_3CH_2(CH_2OH)_3$	7.8	10.4	416	229	—2.0
$C[CH_2OCO(CH_2)_3CH_3]_4$	$CH_3(CH_2)_8CH_3$	0.8	1.1	0.14	0.14	—
»	$CH_3(CH_2)_8CH_2OH$	2.4	3.2	22.9	22.9	—
»	$HOCH_2CH_2CH(OH)CH_3$	2.4	3.2	22.9	50.4	2.6
»	$HOCH_2CH_2CH_2CH_2OH$	2.0	2.7	19.3	30.4	1.5
»	$CH_3CH(OH)CH(OH)CH_3$	2.2	2.9	20.7	70.4	4.1

In the alcohol (hydrocarbon)–diethylene glycol dicaprylate binary system it is possible to employ as the reference value the ratio $k_{p,21}/k_{p,11}$ for n-decane, for which $k_{p,21} = 8k_{CH_2}$ and $k_{p,21}/k_{p,11} = 0.2$, whence $k_{CH_2}/k_{p,11} = 0.025$. The

partial rate constant k_{CH_2OH} can be found from the ratio $k_{p,21}/k_{p,11}$ for *n*-decanol; $k_{CH_2OH}/k_{CH_2} = 84 - 8 = 76$.

Proceeding analogously for the alcohol (hydrocarbon)–pentaerythritol tetravalerate system, we find

$$k_{p,21}/k_{CH_2} = 7.86 \quad (k_{p,21}/k_{p,11})$$

and for the CH_2OH group we have $k_{CH_2OH}/k_{CH_2} = 22.9 - 8 = 14.9$. The ratio k_{CHOH}/k_{CH_2} for the secondary alcohol group can be estimated assuming that the ratio k_{CHOH}/k_{CH_2OH} is the same as for the hexadecane peroxy-radicals, where it is 2.36; we obtain $k_{CHOH}/k_{CH_2} = 2.36 \times 14.9 = 35.2$. Evidently, the ratios k_{CH_2OH}/k_{CH_2} for hexadecane and diethylene glycol dicaprylate are similar (66 and 76), while that for pentaerythritol tetravalerate is significantly lower (15). Since the oxidation of the latter ester results in the preferential formation of peroxy-groups with a quaternary carbon atom in the α-position, the steric effect is apparently the cause of the reduced reactivity of the peroxy-radicals formed from this ester.

Comparison of the calculated ratios $k_{p,21}/k_{CH_2}$ with the value obtained assuming the additivity of the partial rate constants shows that the additivity rule does not hold for polyhydric alcohols; the values of $\Delta\Delta G^{\neq}_{ad}$ vary from −2 to +4 kJ mol^{-1}. Comparison of the estimates obtained by different methods on the whole indicates a satisfactory agreement: in hecadecane $\Delta\Delta G^{\neq}_{ad} > 0$ for the reaction of $RO_2^{\cdot}$ with butane-1,3-diol and $\Delta\Delta G^{\neq}_{ad} = -2.1$ kJ mol^{-1} (Table 4) and −1.7 kJ mol^{-1} (Table 6) for the reaction of $RO_2^{\cdot}$ with 1,1,1-tri(hydroxymethyl)propane. In diethylene glycol dicaprylate the sign and magnitude of $\Delta\Delta G^{\neq}_{ad}$ for the reaction of $RO_2^{\cdot}$ with 1,1,1-tri(hydroxymethyl)propane agree fairly well [−2.0 kJ mol^{-1} (Table 4) and −2.2 kJ mol^{-1} (Table 6)]. The tendency defined by the inequality $\Delta\Delta G^{\neq}_{ad} > 0$ is maintained for the reactions of $RO_2^{\cdot}$ with alcohols in which the hydroxy-groups are located at different carbon atoms of the carbon skeleton and $\Delta\Delta G^{\neq}_{ad} < 0$ for alcohols with the $-C(CH_2OH)_n$ group ($n = 3$).

In the oxidation of unsaturated compounds peroxy-radicals abstract hydrogen atoms from the olefin molecule and add to the double bond. In the oxidation of monomers such as acrylic acid, methacrylic acid, and their esters peroxy-radicals add preferentially to the double bond with formation of polyperoxides.[20] The addition of cumenylperoxy-radicals to the double bonds of a number of unsaturated monoesters and polyesters has been investigated.[21] Each ester (Table 7) was oxidised in the presence of cumenyl hydroperoxide, which was introduced in an amount ensuring the complete replacement of the ester peroxy-radicals by the cumenylperoxy-radicals. The oxidation was carried out at 323 K with azobisisobutyronitrile as the reaction initiator (the initiation rate constant was 2.2×10^{-6} s^{-1}). The process was carried out in a chain regime and the rate of oxidation was measured manometrically, corrections being applied for the evolution of N_2 on decomposition of the initiator and the evolution of O_2 on recombination of the cumenylperoxy-radicals. The reaction scheme (M = monomer) has the following form:

$$\begin{aligned}
&I \rightarrow \dot{r} \xrightarrow{O_2} rO_2^{\cdot} \xrightarrow{ROOH} RO_2^{\cdot} \xrightarrow{M} \dot{M}\ ; \\
&M^{\cdot} + O_2 \rightarrow MO_2^{\cdot}\ ; \\
&MO_2^{\cdot} + HOOR \rightarrow MOOH + RO_2^{\cdot}\ ; \\
&RO_2^{\cdot} + M \xrightarrow{k_p} \dot{M}\ ; \\
&RO_2^{\cdot} + RO_2^{\cdot} \xrightarrow{k_t} ROOR + O_2\ ; \\
&RO_2^{\cdot} + RO_2^{\cdot} \xrightarrow{k_t'} 2RO^{\cdot} + O_2\ ; \\
&RO^{\cdot} + HOOR \rightarrow ROH + RO_2^{\cdot}\ .
\end{aligned} \qquad (i)$$

The rate constants k_p, calculated from the experimental data assuming that the probability of the liberation of radicals into the bulk is 0.5 (Denisov[3]) and with the ratio $k_t'/k_t = 6.3$ (Howard[22]), are listed in Table 7. Comparison of the constants k_p and k_Σ (the latter were calculated assuming additivity) shows that the rule of additivity breaks down also in this group of reactions and to a greater extent the greater the number of ester groups in the molecule.

Table 7. The rate constants for the reaction of cumenyl-peroxy-radicals with the double bonds unsaturated esters (323 K).[21]

Ester	k_p, litre mol^{-1}s^{-1}	k_p/n litre mol^{-1}s^{-1}*	$\Delta\Delta G^{\neq}_{ad}$, kJ mol^{-1}
$CH_3CH{=}CHCOOCH_3$	0.50	0.50	—
$(CH_3)_2C(OCOCH{=}CHCH_3)_2$	0.76	0.38	0.8
$CH_3CH_2C(CH_2OCOCH{=}CHCH_3)_3$	1.05	0.35	1.0
$C(CH_2OCOCH{=}CHCH_3)_4$	1.28	0.32	1.2
$CH_3CH{=}C(CH_3)COOCH_3$ †	1.79	1.79	—
$CH_3CH_2C[CH_2OCOCCH_3{=}CHCH_3]_3$	3.93	1.31	0.9
$C[CH_2OCOC(CH_3){=}CHCH_3]_4$	3.08	0.77	2.3

*The reaction rate constant calculated for one double bond.

IV. THE REACTIONS OF POLYFUNCTIONAL ESTERS WITH HYDROPEROXIDE AND OXYGEN

In the oxidation of organic compounds in the absence of initiators (including hydroperoxide), free radicals are generated via reactions involving molecular oxygen. Three chain initiation and oxidation reactions are known to have been investigated.[23] In the first, O_2 attacks the weakest C–H bond in the molecule with formation of alkyl and hydroperoxy-radicals:

$$RH + O_2 \rightarrow \dot{R} + HO_2^{\cdot}\ .$$

The reaction is endothermic and its heat is $q = -D_{R-H} + 221$ kJ mol^{-1}. In the second, compounds with weak C–H bonds, whose dissociation energy is less than 340 kJ mol^{-1}, enter into a faster termolecular reaction with oxygen:

$$RH + O_2 + HR \rightarrow \dot{R} + H_2O_2 + \dot{R}\ ,$$

whose heat is $q = -2D_{R-H} + 570$ kJ mol^{-1}. In the third, unsaturated compounds combine with oxygen at the double bond to form a biradical:

$$XHC{=}CH_2 + O_2 \rightarrow X\dot{C}HCH_2OO^{\cdot}\ .$$

In the reaction of RH with O_2 the initial species (oxygen, is non-polar, but the R...H...O_2 group, having a non-zero dipole moment, is formed in the transition state. The configuration of the transition state is close to that of the final products ($\dot{R}$ and $HO_2^{\cdot}$) and the dipole moment of $HO_2^{\cdot}$ is 2 D (according to Opeida's estimate[10]). In the reaction of O_2 with a double bond in the transition state a non-polar O_2 molecule is converted into a polar peroxy-radical. It is entirely possible that the formation of the radical is preceded by the formation of an intermediate of the type of the charge-transfer complex $\bar{O}_2...\overset{+}{C}H_2{-}\dot{C}HX$, which has a large dipole moment. In this case too the effect of the multidipolar interaction should be observed.

Studies have been made[24,25] of chain initiation in the oxidation of ethyl propionate (by the mixed initiation method) and diethyl sebacate (by the inhibitor method using the *NN*-di-β-naphthyl-*p*-phenylenediamine inhibitor). In both cases radicals are formed via the bimolecular reaction of oxygen with the ester C–H bonds:

$$v_{i0}=k_{i0}[RH][O_2].$$

The weakest C–H bonds are the α-C–H bonds in the alcohol residue, which in fact make a decisive contribution to initiation. This has been demonstrated by studying the chain initiation in diethyl sebacate deuteriated at the α-C–H bonds of the alcohol residue: deuteriated diethyl sebacate reacts with O_2 much more slowly, as can be seen from a comparison of the values of v_{i0}:[25]

	$10^8 v_{i0}$ (413 K)	$10^8 v_{i0}$ (433 K)
Diethyl sebacate	1.4	5.4
Diethyl [α-D_2] sebacate	0.26	0.7
Kinetic isotope effect	5.2	7.4

Table 8 presents the results of the study of the chain initiation in the aliphatic esters of a number of polyhydric alcohols. It is seen that k_{i0} for pentaerythritol tetrapropionate is approximately twice as high as for the tetraacetate. Consequently the C–H bonds in both the alcohol and acid residues participate in chain initiation. When calculated per ester fragment, the constant k_{i0} varies from ester to ester, i.e. additivity breaks down for this reaction also. A very large difference is observed between the constants k_{i0} for ethyl propionate and diethyl sebacate. An approximately tenfold difference between the k_i is also observed for the addition of oxygen to the double bond in acrylic esters ($\Delta\Delta G^{\neq}_{ad}$ = 7 kJ mol^{-1}).

Table 8. The rate constants for the reactions of oxygen with saturated and unsaturated esters.[24–26]

Ester*	T, K	k/n, litre mol^{-1}s^{-1}	$\Delta\Delta G^{\neq}_{ad}$, kJ mol^{-1}	E, kJ mol^{-1}	A, litre mol^{-1}s^{-1}
$(CH_3)_3CR_2$	423	$6\cdot10^{-7}$	—	—	—
$C_2H_5CR_3$	423	$4\cdot10^{-7}$	—	—	—
CR_4	423	$1.2\cdot10^{-6}$	—	—	—
$C(CH_2OCOCH_3)_4$	423	$6\cdot10^{-7}$	—	—	—
$C_2H_5OCOC_2H_5$	433	$4.7\cdot10^{-3}$	—	133.8	$6.5\cdot10^{13}$
$(C_2H_5)_2[OCO(CH_2)_4]_2$	433	$4.2\cdot10^{-6}$	25.3	141.7	$5.2\cdot10^{11}$
$H_2C{=}CHCOOC_4H_9$	473	$7.6\cdot10^{-7}$		91.6	$5.3\cdot10^{6}$
$(H_2C{=}CHCOOCH_2)_4C$	473	$7.2\cdot10^{-8}$	7.1	180.6	$1.0\cdot10^{18}$

Notation: n is the number of ester groups in the molecule, E the activation energy, and A the pre-exponential factor. *R = $CH_2OCOCH_2CH_3$.

The formation of radicals via this reaction of cumenyl hydroperoxide with the double bonds in polyacrylic esters has been recently studied.[27] The radicals are formed via the reaction

$$ROOH + XHC{=}CH_2 \rightarrow {}^{\cdot}CHXCH_2OH + RO^{\cdot}.$$

As can be seen from the data presented below, a marked deviation from additivity is observed in this reaction also (at 343 K):

Monomer	Methyl acrylate	Tri(hydroxymethyl)-propane triacrylate	Pentaerythritol tetra-acrylate
k, litre mol^{-1}s^{-1}	$1.75\cdot10^{-7}$	$6.1\cdot10^{-8}$	$2.4\cdot10^{-8}$
$\Delta\Delta G^{\neq}_{ad}$, kJ mol^{-1}	0	3.0	5.6

As can be seen from the examples quoted, the deviation from additivity of the partial rate constants is observed for a wide variety of reactions, namely for the reactions of $RO_2^{\cdot}$ with RH (RH = polyhydric alcohol or polyfunctional ester), of $RO_2^{\cdot}$ with $H_2C{\equiv}CHR$, of O_2 with RH, of O_2 with $H_2C{=}CHR$, and of ROOH with $H_2C{=}CHR$. The model which explains these findings is discussed in the next Section.

V. THE MULTIDIPOLAR MODEL OF THE TRANSITION STATE FOR THE REACTION OF A POLAR SPECIES WITH A POLYFUNCTIONAL MOLECULE

We shall consider the possible causes of the deviation from additivity of the partial rate constants for the reactions enumerated above. Substituents in unsaturated compounds are known to exert a mesomeric effect, which is manifested in those cases where the substituent is located in the α-position with respect to the double bond or when there is a system of conjugated double bonds in the molecule. In the examples quoted above (reactions involving pentaerythritol acrylate esters), the ester groups are separated by several C–C bonds, which completely rules out the mesomeric effect as a cause of the deviation from additivity. Furthermore, the same deviation is observed also in the reactions of aliphatic compounds, where there are no double bonds.

The inductive effect is transmitted via σ-bonds; we shall consider whether it can be the cause of the deviation from additivity. Analysis of the structures of molecules for which the above reactions have been investigated shows that the polar groups in the molecule are separated from the reacting bond (C–H or C=C) by four, six, eight, or more σ-bonds. The inductive effect is known to decay already in the second or third C–C σ-bond and for this reason cannot play any role in all the examples quoted above. It affects only the influence of the polar group nearest to the reaction centre and the appearance of additional groups in the molecule no longer involves their inductive effect.

The steric factor is manifested when a bulky group, in particular, a quaternary carbon atom, is present next to the reaction centre. In the pentaerythritol esters, where the peroxy-radical attacks a C–H bond in the alcohol group, this effect apparently occurs. However, it does not explain the change in the partial rate constant for the reaction involving peroxy-radicals (see the Section about the reactions of $RO_2^{\cdot}$ with esters), since, firstly, when the ester group is replaced by an alkyl group in such esters the steric effect is retained, secondly, on passing from a diester to a tetraester, the rate constant increases (Table 2), while the steric effect should reduce it, and, thirdly, in the reactions of $RO_2^{\cdot}$ with dicarboxylic acid esters and with polyhydric alcohols (Tables 3, 4, and 6) there is no steric hindrance to attack and yet the deviation from additivity does occur.

Thus the three effects examined above do not explain the deviations of the partial rate constants from additivity, which are frequently encountered experimentally. The most probable and possibly the only cause is the effect of the electrostatic interaction of the polar groups in the molecule and the influence of the field which they generate on the transition state. The point is that, in all the examples examined, the molecule containing functional groups is either attacked by polar species ($RO_2^{\cdot}$, ROOH) or forms a polar transition state, as in the reactions involving oxygen. Evidently the attack of a polar species on a polyfunctional molecule is accompanied by an electrostatic interaction, whose energy depends on the dipole moments and the disposition of these groups.

These simple considerations were used as the basis for the concept of the multidipolar interaction in the reactions of polyfunctional compounds.[6] From the standpoint of electrostatic interactions, a polyfunctional molecule constitutes a multidipole, i.e. a set of interacting dipoles. We shall consider such a molecule, containing n functional groups, as a set of interacting dipoles with dipole moments μ_1, μ_2, ..., μ_n. These dipoles rotate as a result of the rotation of the molecular fragments, but they cannot assume any arbitrary mutual orientation, because their rotation is limited by the condition that the valence angles and the internuclear distances in the molecule remain constant.

Thus a polyfunctional molecule considered in this way consists of a semirigid skeleton made up of atoms in which groups (dipoles) having a limited mobility are located at specific sites. If the polar groups are separated by several C–C bonds (two and more), then the distance between the centres of the dipoles will exceed the length of each group (dipole). The energy of the interaction of such dipoles can be described with an adequate approximation by the formula for the interaction of two point dipoles:[28]

$$U_{ij}\ (\text{kJ mol}^{-1}) = 60\,(\mu_i\mu_j N_A/\varepsilon r_{ij}^3)\,[\sin\theta_i \sin\theta_j \cos(\varphi_j - \varphi_i) - 2\cos\theta_i \cos\theta_j] \quad (1)$$

where N_A is the Avogadro number, ε the dielectric constant of the medium, θ_i and θ_j are the angles of inclination of the polar axes of the dipoles i and j relative to the line connecting their centres, and ϕ_i and ϕ_j are the angles between the polar axes of the dipoles and the perpendicular lines drawn through their centres; μ is expressed in Debyes (D) and r in Ångstroms (Å). The energy of the interaction at the dipoles is correspondingly equal to the sum of the energies of the pair interactions ($i \neq j$):

$$U_n = \frac{1}{2}\sum_i \sum_j U_{ij} \ . \quad (2)$$

In order to estimate the value which the energy of such an interaction can assume, we shall consider several examples. Suppose that $\varepsilon = 1$, that all the dipolar groups have a dipole moment of 2 D, and that all the r_{ij} are also equal.

(1) If $n = 2$ and $r = 3$ Å, then $U_{\min} = -18$ kJ mol^{-1} and $U_{\max} = 18$ kJ mol^{-1}.

(2) If $n = 2$ and $r = 4$ Å, then $U_{\max} = 7.5$ kJ mol^{-1}.

(3) If $n = 3$, $r = 4$ Å, and the dipoles are located at the vertices of a triangle, then $U_{\max} = 20$ kJ mol^{-1}.

(4) If $n = 4$, $r = 4$ Å, and the dipoles are located at the vertices of a square, then $U_{\max} = 28$ kJ mol^{-1}.

The activation energy for radical abstraction reactions varies in most cases in the range from 10 to 60 kJ mol^{-1}. Consequently the energy of the dipole–dipole interaction is comparable to the activation energy for radical reactions. When a molecule of this kind is attacked by a species having a dipole moment, a conglomerate consisting of $n + 1$ dipoles arises in the transition state, which also represents a set of point dipoles, the interaction energy of which is described by the expression

$$U_{n+1} = \frac{1}{2}\sum_i^{n+1} \sum_j^{n+1} U_{ij} \ . \quad (3)$$

The contribution of the multidipolar interaction to the Gibbs free energy of activation is

$$\Delta G_\mu^{\neq} = N_A\,(U_{n+1} - U_n) \ . \quad (4)$$

If the mutual orientations of the polar groups of the molecules and the distances between them are similar in the initial and transition states, we obtain

$$\Delta G_\mu^{\neq} = \frac{N_A \mu^*}{\varepsilon} \sum_i^n \frac{\mu_i}{r_i^3} f(\theta^*, \theta_i, \varphi^*, \varphi_i) \ , \quad (5)$$

where the asterisk refers to the polar group of the attacking species. The component of the Gibbs free energy of activation $\Delta G_\mu^{\neq}$, due solely to the dipole–dipole interaction, is defined by the simple relation[29]

$$\Delta G_\mu^{\neq} = RT \ln(k_0/k) \ . \quad (6)$$

The difference between the energies of the multidipolar interaction in the transition state and in the initial molecule may be both positive and negative. A monofunctional compound can be used as a reference. In this case k_0 already takes into account the dipole–dipole interaction and the formula $\Delta G_\mu^{\neq} = RT \ln(k_0/k)$ reflects the influence of the multidipolar interaction after the subtraction of the interaction of the attacking species with the field of the attacked reaction centre (the dipole–dipole pair interaction).

The relation between $\Delta G_\mu^{\neq}$ and the experimental activation energy E and the experimental pre-exponential factor A can be found in the following way. Since $E = RT^2 \mathrm{d}\ln k/\mathrm{d}T$ and $\ln k = \ln k_0 - \Delta G_\mu^{\neq}/RT$, we obtain

$$E = E_0 + \Delta G_\mu^{\neq} - T\mathrm{d}\Delta G_\mu^{\neq}/\mathrm{d}T \ . \quad (7)$$

The temperature dependence of E is due to two factors. Firstly, $\Delta G_\mu^{\neq} = \Delta G_{\mu 1}^{\neq}/\varepsilon$; the dielectric constant ε varies with temperature in accordance with the exponential function

$$\varepsilon = \varepsilon_0 e^{-L_\varepsilon T} \ .$$

Secondly, the extent of the rotation of the molecular fragments and the amplitude of the deformation vibrations of the bonds increase with increase of temperature. The mutual orientation of the dipoles is correspondingly averaged out and $\Delta G_{\mu 1}^{\neq}$ diminishes.

If the molecule is regarded as a microdielectric, one can assume that $\Delta G_{\mu 1}^{\neq}$ is related to temperature (like ε) in the following way:

$$\mathrm{d}\ln \Delta G_{\mu 1}^{\neq}/\mathrm{d}T = -L_G \ .$$

After substitution of the expressions for $\Delta G_\mu^{\neq}$ in Eqn.(7) and differentiation, we obtain

$$E = E_0 + \Delta G_\mu^{\neq} + T(L_G - L_\varepsilon)\Delta G_\mu^{\neq} \ .$$

Since the entropy is linked to the Gibbs free energy by the relation $\Delta S = -\mathrm{d}\Delta G/\mathrm{d}T$, we obtain for the change in the activation entropy as a result of the multidipolar interaction

$$\Delta S_\mu^{\neq} = -\mathrm{d}\Delta G_\mu^{\neq}/\mathrm{d}T = (L_G - L_\varepsilon)\Delta G_\mu^{\neq} \ . \quad (8)$$

On the other hand, $\Delta S_\mu^{\neq}$ can be estimated from the pre-exponential factor: since $\Delta S^{\neq} = R \ln A + \text{const.}$, we obtain

$$\Delta S_\mu^{\neq} = R \ln(A/A_0) \ . \quad (9)$$

Using Eqns.(7)–(9), we have

$$\Delta G_\mu^{\neq} = \frac{E - E_0}{1 + \ln(A/A_0)/\ln(k_0/k)} \ , \quad (10)$$

$$L_G = L_\varepsilon + T^{-1}[\ln(A/A_0)/\ln(k_0/k)] \ . \quad (11)$$

The conclusions which follow from the model of the multidipolar transition state examined above are compared with the experimental data in the next Section.

The influence of polar groups on the energy of the transition state partly resembles solvation, but there are two significant differences. Firstly, solvent molecules approach closely the polar transition state (reaction centre) and surround it, whereas the polar groups of the polyfunctional molecule exert their influence via a field over a certain distance. Secondly, the molecules solvating the polar group (including the reaction centre) are oriented in the energetically most favourable manner, whereas the orientation of the groups in a polyfunctional molecule is restricted by the specific disposition of the atoms and groups in it.

The dipole–dipole interaction can also exert a more profound influence on the transition state, apart from establishing a specific electrostatic potential. If readily polarisable bonds (π-bonds, atoms with p and d electrons), which are polarised in the transition state, participate in the reaction, then the polar groups in the molecule can influence the polarisation of the transition state, which can lead to an intensification of the effect of the multidipolar interaction and to a greater deviation from additivity. Finally, in those cases where the reaction proceeds with electron transfer and in the transition state a neutral species is converted into an ion (ion pair), the result should be a stronger and longer-range ($U \propto r^{-2}$ instead of $U \propto r^{-3}$) ion–dipole interaction and correspondingly a higher value of $|\Delta G_{\mu}^{\neq}|$.

VI. ANALYSIS OF EXPERIMENTAL DATA WITHIN THE FRAMEWORK OF THE CONCEPT OF THE MULTIDIPOLAR INTERACTION IN THE TRANSITION STATE

It follows from the model of a polyfunctional molecule as a system of interacting groups (dipoles) that, in those cases where such a molecule is attacked by a non-polar species, the ion–dipole interaction potentials in the molecule and in the activated complex are the same or very similar, so that the rule of the additivity of the partial rate constants should hold. As we have seen, the rule breaks down for the reactions of $RO_2^{\cdot}$ with a series of esters of pentaerythritol and its analogues (Table 2).

The rate constants for the reactions of trichloromethyl radicals with these esters have been measured.[30] The reactions were investigated in CCl_4 at 373 K using benzoyl peroxide as the initiator. It was continued until the consumption of the peroxide was complete. The amounts of chloroform and hexachloroethane formed were determined by gas–liquid chromatography. The reactions taking place in the initiator (I)–ester (RH)–CCl_4 system are described by the following scheme:

$$I \xrightarrow{k_d} \dot{r} + \dot{r} \xrightarrow{k_t} 2\dot{r}\,,$$
$$\dot{r} + CCl_4 \rightarrow rCl + \dot{C}Cl_3\,,$$
$$\dot{C}Cl_3 + RH \xrightarrow{k_p} CCl_3H + \dot{R}\,,$$
$$\dot{R} + CCl_4 \rightarrow RCl + \dot{C}Cl_3\,,$$
$$\dot{C}Cl_3 + \dot{C}Cl_3 \xrightarrow{k_t} C_2Cl_6\,.$$

According to this scheme, the amount of hexachloroethane formed at the end of the experiment corresponds to the amount of free radicals produced on decomposition of benzoyl peroxide. The reaction has a chain mechanism and the average chain length varies from 3 to 40 units. The rate constant ratio $k_p(2k_t)^{-1/2}$ was determined from the amount of $CHCl_3$ formed. The absolute value of k_p was calculated on the assumption that $2k_t = 3.1 \times 10^9$ litre mol^{-1} s^{-1}.[31] The experimental conditions and the values of $k_p(2k_t)^{-1/2}$ and k_p are listed in Table 9. The results make it possible to calculate and compare the partial rate constants for the reactions of dichloromethyl radicals with the $-CH_2OCOCH_2CH_3$ fragment for different numbers of ester groups in the molecule.

It is seen from the data in Table 9 that the k_p calculated per fragment are close for all three propionates regardless of the number of ester fragments in the molecule. Thus, to a first approximation, the rule of additivity holds for the reactions of trichloromethyl radicals with polyfunctional esters. The trichloromethyl radical is an electrophilic species, like the peroxy-radical. When the inductive effect is a possible cause of the deviation from additivity, such deviation would therefore have been observed also for the $\dot{C}Cl_3$ radicals, as happens for peroxy-radicals. The validity of the rule of additivity for radicals in the case of $\dot{C}Cl_3$ demonstrates that in this instance the inductive effect does not play a significant role. The transition state in the case where a C–H bond is attacked by $\dot{C}Cl_3$ apparently has a low dipole moment, which does not exceed 0.5 D. The energy of the interaction of the ester groups in such a dipole is low and its effect on k_p is within the limits of the accuracy of the measurement (for comparison, we may recall that the dipole moment of the peroxy-radical is ~2 D). An analogous result has been obtained for the reactions of non-polar undecyl radicals with monoesters and polyesters[11] (Table 10). The reactivity of the esters has been investigated by the method of competing reactions:

$$C_{11}H_{23}^{\cdot} + RH \xrightarrow{k_1} C_{11}H_{24} + R^{\cdot}\,,$$
$$C_{11}H_{23}^{\cdot} + O_2 \xrightarrow{k_2} C_{11}H_{23}OO^{\cdot}\,.$$

Table 9. The rate constants for the reactions of trichloromethyl radicals with esters (373 K, CCl_4).[30]

Ester	$10^3 k_p(2k_t)^{-1/2}$, litre$^{1/2}$mol$^{-1/2}$s$^{-1/2}$	k_p, litre mol^{-1}s^{-1}	k_p/n, litre mol^{-1}s^{-1}
$C(CH_2OCOCH_2CH_3)_4$	2.8±0.1	160	40
$C[CH_2OCO(CH_2)_8CH_3]_4$	22.3±0.4	1250	—
$(CH_3)_2C(CH_2OCOCH_3)_2$	1.8±0.1	100	50
$CH_3CH_2C(CH_2OCOCH_2CH_3)_3$	3.1±0.5	170	43

The source of undecyl radicals was dilauryl peroxide, which was decomposed in chlorobenzene in the presence of the ester RH in an atmosphere of oxygen. The intensity of the first reaction was inferred from the yield of undecane relative to the decomposed peroxide. Table 10 shows that the relative rate constants for the reactions of the alkyl radical with the esters calculated per group differ by not more than 15%.

Table 10. The rate constants for the reactions of undecyl radicals with esters (373 K, C_6H_5Cl).[11]

Ester	$10^4 (k_1/k_2)$	$10^4 (k_1/nk_2)$
$CH_3(CH_2)_4COOCH_3$	1.1	1.1
$CH_3OCO(CH_2)_8COOCH_3$	1.8	0.9
$CH_3(CH_2)_4COOCH(CH_3)_2$	1.2	1.2
$(CH_3)_2CHOCO(CH_2)_8COOCH(CH_3)_2$	2.2	1.1
$CH_3(CH_2)_3COOCH_2CH_3$	1.3	1.3
$[CH_3(CH_2)_3COOCH_2]_4C$	6.8	1.7

The deviation of the partial rate constants from additivity is thus observed only in those cases where the molecule is attacked by polar species ($RO_2^{\cdot}$, ROOH) or when a polar transition state is formed (in reactions with O_2). It follows from Eqn.(4) that the component $\Delta G_{\mu}^{\neq}$ due to the dipole–dipole interaction can be both positive when $U_{n+1} > U_n$ and negative when $U_{n+1} < U_n$, i.e. the deviations from additivity can be both towards a decrease and an increase of the reaction rate constant compared with the sum of the partial rate

constants. Indeed both cases have been observed experimentally (Table 11), but there are more examples with $\Delta G_{\mu}^{\neq} > 0$.

Table 11. The sign of the multidipolar effect ($\Delta G_{\mu}^{\neq}$) in various radical reactions.

Radical*	Molecule	Sign
$C_6H_5(CH_3)_2COO^{\cdot}$	$ROCO(CH_2)_nCOOR$	+
$C_6H_5(CH_3)_2COO^{\cdot}$	$ROCO(CH_2)_2COOR$	+
$C_6H_5(CH_3)_2COO^{\cdot}$	$ROCO(CH_2)_2O(CH_2)_2COOR$	+
$C_6H_5(CH_3)_2COO^{\cdot}$	$(CH_3)_{4-n}C(CH_2OCOCH_2CH_3)_{n-4}$	−
$C_{16}H_{35}OO^{\cdot}$	$HOCH_2(CH_2)_nCH_2OH$	+
$C_{16}H_{35}OO^{\cdot}$	$R_{4-n}C(CH_2OH)_n$	−
$RO_2^{\cdot}$	$HOCH_2(CH_2)_nCH_2OH$	+
$RO_2^{\cdot}$	$R_{4-n}C(CH_2OH)_n$	−
$C_6H_5(CH_3)_2COO^{\cdot}$	$R_{4-n}C[CH_2OCOC(CH_3)=CH_2]_n$	+
O_2	$C[CH_2OCOC(CH_3)=CH_2]_4$	+
$C_6H_5(CH_3)_2COOH$	$C[CH_2OCOHC=CH_2]_4$	+

*Here $RO_2^{\cdot}$ is the radical derived from diethylene glycol dicaprylate.

It follows from Eqns.(4) and (5) that $\Delta G_{\mu}^{\neq}$ is lower the further is the reaction centre from the polar groups. This conclusion has been tested in relation to the reactions of $RO_2^{\cdot}$ with pentaerythritol esters.[14] In the molecule of such an ester the radical $RO_2^{\cdot}$ attacks both the C–H bonds of the alcohol residue, located near the ester groups, and the C–H bonds of the acid residue. The greater the number of CH_2 groups in the acid residue, the greater the contribution of the CH_2 groups remote from the polar ester groups to the overall reaction rate constant. With increase of the number of methylene groups in the acid residue of the ester, the rate constant calculated per CH_2 group should therefore appraoch that of an n-paraffin, which has in fact been confirmed by experimental data:[14] $k_{CH_2} = 1.4$ litre mol^{-1} s^{-1} (407 K) for pentaerythritol tetrapropionate, 2.7 litre mol^{-1} s^{-1} for pentaerythritol tetracaprate, and 2.8 litre mol^{-1} s^{-1} for n-heptadecane. It is seen that, with increase in the number of CH_2 groups, the deviation from additivity diminishes as the distances of the attacked group from the dipolar groups are increased.

Table 12. The parameters* of the multidipolar interaction in the reactions of cumenylperoxy-radicals with the esters of mono- and di-carboxylic acids.[4]

Ester	k (413 K)	$\Sigma k_{pl}^{\prime\prime}$	$\Delta G_{\mu}^{\neq}$, from Eqn.(6)	E	lg A	$\Delta G_{\mu}^{\neq}$, from Eqn.(10)	$\Delta S_{\mu}^{\neq}$	L_G
$CH_3CH_2COOCH_3$	92	—	—	29	5.63	—	—	—
$CH_2(CH_2COOCH_3)_2$	7.2	185	11.1	69	9.58	11.8	76	9.3
$CH_3CH_2COOC_2H_5$	18	—	—	37	5.93	—	—	—
$CH_2(CH_2COOC_2H_5)_2$	7.0	37	5.6	69	9.57	6.0	70	14.4
$CH_3CH_2COOC(CH_3)_3$	8.9	—	—	53	7.65	—	—	—
$CH_2[CH_2COOC(CH_3)_3]_2$	2.6	185	6.6	73	9.65	5.7	38	9.6

*k and A are expressed in litre mol^{-1} s^{-1}, E and $\Delta G_{\mu}^{\neq}$ in kJ mol^{-1}, and $\Delta S_{\mu}^{\neq}$ in J mol^{-1} K^{-1}.

Table 12 presents the values of E and lg A for the reactions of peroxy-radicals with monoesters and polyfunctional esters. In all the cases quoted, the compensation effect is observed: with increase of the activation energy, the pre-exponential factor also increases. The concept of the multidipolar interaction explains this effect; within its framework, the effect is characterised by the coefficient L_G [see Eqns.(7)–(11)]. The physical significance of this compensation consists in the fact that, owing to the intensification of the torsional and deformation vibrations of the groups in the molecule as the temperature rises, the value of $|\Delta G_{\mu}^{\neq}|$ decreases.

Table 12 shows that the $\Delta G_{\mu}^{\neq}$ obtained by two different methods agree satisfactorily. Since the manifestation of the effect of the multidipolar interaction requires as an obligatory condition that one of the reactants should contain several polar groups, it follows that the effect should also appear when a radical containing several polar groups interacts with the polar molecule. Data of this kind have been obtained in the studh of the kinetics of the oxidation of mono- and tetra-functional unsaturated esters in the presence of ionol as the inhibitor. The rate constant for the reaction of peroxy-radicals with ionol was calculated from the experimental data (Table 13). They show that the peroxy-radical containing four ester groups attacks ionol ~4 times more slowly than one having a single ester group; $\Delta G_{\mu}^{\neq} \cong 4$ kJ mol^{-1}. The fact that in this instance the above difference is caused by the dipole–dipole interaction has been confirmed by experiments on the coupled oxidation of the same esters with cumene, from which the rate constants for the reactions of the same peroxy-radicals with the weakly polar cumene were obtained ($\mu = 0.4$ D for cumene and 1.6 D for ionol). The data in Table 13 show that the rate constants for the reactions of the above radicals with the non-polar cumene are very similar.

Table 13. The rate constants for the reactions of mono- and poly-functional peroxy-radicals of monomers with ionol (k_2, 323 K) and cumene (k_1, 343 K).

Monomer	k_1, litre $mol^{-1}s^{-1}$	k_2, litre $mol^{-1}s^{-1}$	$\Delta G_{\mu}^{\neq}$, kJ mol^{-1}
$CH_3OCOHC=CH_2$	1.2	$8.1\cdot10^3$	—
$(H_2C=CHCOOCH_2)_4C$	1.0	$1.9\cdot10^3$	4.1
$CH_3OCO(CH_3)C=CH_2$	0.7	$3.8\cdot10^3$	—
$[H_2C=C(CH_3)COOCH_2]_4C$	0.8	$1.1\cdot10^3$	3.5

The important factor is the heat of reaction, on which depends not only the activation energy but also the configuration of the activated complex. According to Hammond's postulate,[2] the configuration is closer to that of the reaction products the more endothermic the reaction. In its turn, the higher the heat of reaction, then, other conditions being equal, the weaker the reflection of the structural factors in the reaction rate constant. We shall consider how this tendency is manifested in the reactions of polyfunctional molecules. The comparison can be carried out for peroxy-radicals, hydroperoxide, and oxygen in their reactions with unsaturated compounds. The dipole moments of $RO_2^{\cdot}$ and ROOH are similar and oxygen, having added to the double bond, also produces a peroxy-radical. On the other hand, these reactants differ sharply in their reactivities, which can be seen from a comparison of the rate constants for the

above reactions. The reactions and the values of ΔH^0 calculated for them are presented below (on the basis of the data in Kondrat'ev's handbook[7]):

$$CH_3OO^{\cdot} + H_2C{=}CH_2 \rightarrow CH_3OOCH_2CH_2^{\cdot} \quad (\Delta H^0 = -46 \text{ kJ mol}^{-1});$$
$$CH_3OOH + H_2C{=}CH_2 \rightarrow CH_3O^{\cdot} + HOCH_2CH_2^{\cdot} \quad (\Delta H^0 = 30 \text{ kJ mol}^{-1});$$
$$O_2 + H_2C{=}CH_2 \rightarrow {}^{\cdot}OOCH_2CH_2^{\cdot} \quad (\Delta H^0 = 130 \text{ kJ mol}^{-1}).$$

The peroxy-radicals also differ in their reactivities in addition reactions: the $RO_2^{\cdot}$ derived from styrene is much more reactive than the $RO_2^{\cdot}$ derived from acrylates. The rate constants from the values of ΔH^0 and $\Delta G_{\mu}^{\neq}$ in reactions involving addition to the double bond in tetra-acrylate esters are compared below:

Reactant	$RO_2^{\cdot}$(styrene)	$RO_2^{\cdot}$(acrylate)	$C_6H_5(CH_3)_2COOH$	O_2
T, K	323	323	343	343
k, litre mol^{-1}s^{-1}	101	0.8	$2.4\cdot10^{-6}$	$4\cdot10^{-10}$
ΔH^0, kJ mol^{-1}	−46	—	30	130
$\Delta G_{\mu}^{\neq}$, kJ mol^{-1}	0.5	1.2	5.6	13.8

Evidently the effect of the multidipolar interaction is indeed manifested in the above series of reactions to a greater extent the more endothermic the reaction.

We have seen that the energy of the dipole–dipole interaction depends on the dipole moment of the species, their orientation, and the distance between them. For a distance of 4 Å and a dipole moment of 2 D, the absolute differences between the interaction potentials are $|U_{N+1} - U_n|_{max} =$ 12.5 kJ mol^{-1} ($n = 2$) and 8 kJ mol^{-1} ($n = 3$), as shown above. Thus the maximum energy of the multidipolar interaction is ~10 kJ mol^{-1} and $\Delta G_{\mu}^{\neq}$ can vary in the range from 0 to 10 kJ mol^{-1}. The data presented in Tables 4, 6, 7, 8, 12, and 13 show that the $\Delta\Delta G_{ad}^{\neq}$ do not as a rule exceed 10 kJ mol^{-1} and in most cases are in the range from 2 to 4 kJ mol^{-1}. There is only one exception: the data for the reactions of oxygen with esters of mono- and di-carboxylic acids (Table 8), where $\Delta\Delta G_{ad}^{\neq} = 25$ kJ mol^{-1}. This enormous difference between the rate constants is clearly outside the framework of the effect of the multidipolar interaction and its cause remains obscure.

For the reactions of unsaturated compounds with oxygen (Table 8) and a hydroperoxide, the $\Delta\Delta G_{ad}^{\neq}$ (7 and 5 kJ mol^{-1}) are apparently higher than the $\Delta G_{\mu}^{\neq}$ determined solely by the interaction of these groups as rigid dipoles (in these reactions the distance of the reaction centre from the ester groups is 5–6 Å and the energy of the dipole–dipole interaction is in this instance 2–3 kJ mol^{-1}). However, only a readily polarisable π-bond is involved in the above reaction; the polarisation of this bond contributes to $\Delta G^{\neq}$ and the observed $\Delta\Delta G_{ad}^{\neq}$ apparently includes both the energy of the electrostatic interaction of the dipolar groups and the difference between the polarisations of the reacting bond under the influence of the polar groups in mono- and poly-functional esters. One cannot rule out also a longer-range ion–dipole interaction when the reactions take place with electron transfer via the activated complexes $O_2^{\ddot{-}}...\dot{C}H_2{-}\overset{+}{C}OOR$ and $ROOH^{\ddot{-}}...\dot{C}H_2{-}\overset{+}{C}OOR$.

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Thus the extensive experimental data for the reactions of $RO_2^{\cdot}$, ROOH, and O_2 with saturated and unsaturated polyesters as well as the reaction of the polyfunctional radical $RO_2^{\cdot}$ with ionol show convincingly that the deviations from additivity are in almost all cases a consequence of the electrostatic interaction of the polar groups as a set of dipoles. In the case of unsaturated compounds this effect is enhanced by the influence of the polar groups on the polarisation of the π-bonds in the transition state.

As shown above, the effect of the multidipolar interaction is characteristic of the reactions of polyfunctional compounds and apparently plays an important role in the reactions of polymers containing functional groups and biopolymers.

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Activation of Molecular Oxygen by Metal Complexes and Its Role in the Mechanism of Liquid Phase Oxidation

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Problems of the involvement of molecular complexes of oxygen with variable-valence metal compounds in the liquid-phase oxidation of organic compounds, including the chain initiation reactions in radical chain oxidation, via the interaction of such complexes with the hydrocarbon are considered. The possibility of the operation of mechanisms resembling those of enzymic oxidation is analysed. Despite the lack in many instances of unambiguous evidence for the occurrence of the oxidation reaction via a mono- or di-oxygenase mechanism, one can assume that the reaction conditions and mechanisms in many chemical systems are close to those in biological systems.
The bibliography includes 119 references.

CONTENTS

I. Introduction 875
II. Initiation of oxidation chains by variable-valence metal superoxo-complexes 876
III. The monoxygenase oxidation mechanism 877
IV. Models of the action of dioxygenases 881

I. INTRODUCTION

The catalytic oxidation reactions of organic substances in the liquid phase constitute one of the commonest types of chemical reactions. The study of their mechanisms is important both for the creation of new selective processes in chemical technology and for the understanding of many biochemical processes.

The liquid-phase catalytic oxidation reactions of organic substances in the presence of the majority of variable-valence metal compounds proceed via a radical chain mechanism.[1-3] The catalyst can then participate in all the elementary oxidation stages—chain branching, chain propagation, and chain termination. The acceleration of the catalytic reaction compared with the non-catalytic reaction is associated mainly with the increase of the rate of chain branching as a result of the radical decomposition of hydroperoxides by variable-valence metal compounds.[4]

When the oxidation reaction has a radical chain mechanism, the introduction of homogeneous or heterogeneous catalysts can influence the selectivity of the oxidation through interaction of the catalyst with free radicals, which in many instances alters both the rate and the composition of the chain propagation reaction products.

The ratio of the oxidation products can also vary owing to alteration of the chain length. Since an increase of free radical formation rate in the presence of the catalyst entails a decrease of the oxidation chain length, the free radical recombination products accumulate in large amounts in these oxidation reaction mixtures.[5]

The use of metal complexes as oxidation catalysts, which have a fairly pronounced peroxidase function, is usually complicated by the rapid oxidation of the ligand by peroxides or free peroxy-radicals,[6-8] which leads to the replacement of the ligand in the early stages of the oxidation process and hence can alter the oxidation reaction pathway in the course of the reaction.

Evidently the involvement of active free radicals in catalytic liquid-phase oxidation reactions cannot ensure a sufficiently high process selectivity because of the high reactivity, which leads to a large number of different reactions of the starting materials and the intermediates.

Nevertheless, in the words of Academician N.M.Emanuel', "the problem of the effective employment of natural raw materials is of prime importance in the chemistry of our time. The high selectivity and rate of a chemical reaction accompanied by small energy expenditures and in apparatus of minimal size have become the principal criteria of the likely usefulness of the chemical process from the practical point of view".[5]

From the standpoint of the increased selectivity of the oxidation reactions, the creation of conditions ensuring the direct insertion of oxygen in a C–H bond of the molecule of the organic substance with formation of alcohols, hydroperoxides, and other oxygen-containing compounds would be most promising.

In the absence of a catalyst, oxygen, which exists in a triplet ground state, is incapable of reacting with substrates in the singlet state because such a process infringes the spin conservation rule. The formation of molecular complexes of oxygen with variable-valence metal compounds removes the spin restriction and the direct reaction of oxygen with the substrate accompanied by the formation of hydroperoxides,

$$RH+O_2 \rightarrow ROOH$$

or alcohols,

$$RH_2+O_2+DH_2 \rightarrow HROH+H_2O+D \quad , \qquad (1)$$

where DH_2 is a cofactor (or cosubstrate), which serves as the reducing agent, becomes possible, in principle, in this system.

The problem of the activation of molecular oxygen by variable-valence metal complexes has been the subject during the last decade of numerous investigations devoted to various aspects of the structure of such complexes,[9,10] their reactivity, and the mechanism of their interaction with substrates undergoing oxidation.[11-15]

Variable-valence metal compounds readily interact in many instances with molecular oxygen, forming adducts in which oxygen is present in the form of the superoxide ion O_2^- or the peroxide ion O_2^{2-}. The peroxo-complexes can in their turn contain either one metal atom (when the metal can serve as a donor of two electrons, $M\begin{smallmatrix}O\\|\\O\end{smallmatrix}$) or two metal atoms (for metals which undergo a change in valence only by unity, the μ-peroxo-complexes M–O–O–M). Metal oxo-complexes (M=O) and μ-oxo-complexes (M–O–M), containing one oxygen atom, can also be formed. However, such complexes

are as a rule inactive in oxygen transfer processes. From the standpoint of their employment as oxidants, transition metal peroxo- and super-oxo-complexes of oxygen are the most promising.

II. INITIATION OF OXIDATION CHAINS BY VARIABLE-VALENCE METAL SUPEROXO-COMPLEXES

Despite the large number of studies which have been made on the mechanisms of the activation of molecular oxygen, it is at present fairly difficult to relate the mechanism of the oxidation of organic substances in the presence of complexes of molecular oxygen with the catalyst to the structure of such complexes. It has been suggested that paramagnetic mononuclear complexes of the type $M...O_2^-$ (superoxo-complexes) can serve as electron transfer agents:[16,17]

$$RH_2 + M \cdots O_2^- \rightarrow M \cdots O_2^{2-} + RH_2^+$$

or can participate in the radical substitution reaction[15]

$$RH_2 + M \cdots O_2^- \rightarrow M \cdots HO_2^- + RH^\cdot \qquad (2)$$

and can thus ensure the initiation of radical chain reactions.

The reactions of O_2^- coordinated in the titanium(IV) coordination sphere to various organic substrates have been investigated by EPR using a flow technique.[17] Although the authors did in fact observe that only compounds with comparatively weak C–H, N–H, or O–H bonds, such as *p*-toluidine, *p*-aminophenol, and 3,5-dihydroxybenzaldehyde, react with the complex $Ti(IV).O_2^-$, a direct relation between the rate of reaction and the bond dissociation energy apparently does not exist. Thus the dissociation energy of the C–H bond in toluene is approximately equal to the O–H bond energy in phenol, while the C–H bond energy in benzaldehyde is significantly lower. Nevertheless, only phenol is oxidised in the process of $Ti(IV).O_2^-$.

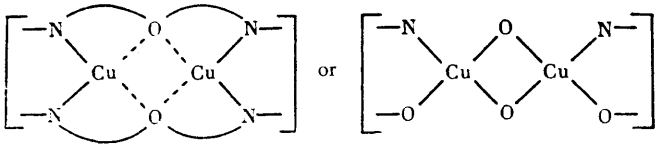
At the same time, a satisfactory quantitative correlation has been observed between the reaction rate constant and the ionisation potential of the substrate. The results obtained made it possible to suggest that at least in aqueous solutions at room temperature the rates of the radical substitution reactions (2) of the complexes $Ti(IV).O_2^-$ [17] and $Zr(IV).O_2^-$ [18] are negligibly low compared with the rate of electron transfer with formation of the coordinated dianion $Ti(IV).O^{2-}$ and the radical-cation of the substance being oxidised:

$$Ti(IV) \cdot O_2^- + RH_2 \rightarrow Ti(IV) \cdot O_2^{2-} + RH_2^+ .$$

The rate constants for the interaction of the complex $Zr(IV).O_2^-$ with amines and phenols are close to the corresponding constants for the complex $Ti(IV).O_2^-$.[18]

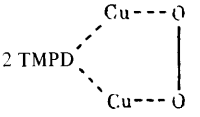
The oxidation of *NNN'N'*-tetramethyl-*p*-phenylenediamine (TMPD) by oxygen in the presence of square planar complexes of bivalent cobalt, such as the cobalt complexes of Schiff bases (CoL_2), leads to the formation of a coloured compound, whose electronic spectrum is the same as that of the complex $[Cl(L)_2TMPD^+]$.[16] Electron transfer takes place only in the joint presence in the solution of TMPD, O_2, and $Co(L)_2$, which suggests that the reaction proceeds in a ternary complex via a concerted mechanism.

Dinuclear copper complexes with chelate units



in which the distance between the copper atoms is not less than 3–3.5 Å, exhibit a high catalytic activity in the oxidation of TMPD by molecular oxygen.[19] The catalytic activity of these complexes is determined by their reduction potential: the more positive the reduction potential, the higher the activity of the catalyst.

Increasing the distance between the copper atoms above 3.5 Å causes the catalytic activity of the complex to fall rapidly. The maximum initial rate of oxidation is attained for the ratio [TMPD] : [catalyst] = 2 : 1. It has been suggested that the oxidation proceeds with two-electron reduction of oxygen to O_2^{2-} via an intermediate stage in which is produced the complex



The transfer of two electrons in such a complex can occur in one stage via a concerted mechanism.[19]

Despite the fact that at room temperature in aqueous solutions[17] the rate of electron transfer is probably significantly higher than the rate of the radical substitution reaction (2), chain initiation via reaction (2) can take place at least in the presence of certain copper, nickel, and coblat complexes.

The problem of demonstrating the involvement of complexes of molecular oxygen with variable-valence metal compounds in the oxidation chain initiation stage in many cases cannot be solved unambiguously primarily because almost all variable-valence metal compounds can decompose hydroperoxides into free radicals at rates greatly exceeding the rate of formation of radicals via reaction (2), which creates considerable difficulties for the identification of reaction (2) against the background of chain branching even in the presence of traces of hydroperoxides and imposes particularly stringent requirements on the degree of elimination of traces of hydroperoxides from hydrocarbons. In order to reach clear-cut conclusions about the role of reaction (2) in the oxidation process, it is necessary to carry out a quantitative comparison of the observed rates of oxidation with the rates which can be ensured by chain branching in the presence of the catalyst.

In addition, there are virtually no unambiguous methods whereby one could demonstrate a non-radical reaction pathway. The method of inhibitors widely employed in non-catalytic oxidation frequently fails to yield information in the presence of catalysts because, on the one hand, inhibitors (phenols or aromatic amines) can behave as promoting agents, or catalytic poisons, forming complexes with the catalyst, and, on the other hand, for sufficiently high rates of chain initiation, large concentrations of the inhibitor must be introduced into the reaction in order to obtain effects beyond experimental error, which can lead to its intense oxidation by oxygen. Thus, when the method of inhibitors is used to investigate the mechanism of catalytic oxidation, in each individual case it is necessary to have evidence that the inhibitor reacts in the given catalytic system only with the free radicals (i.e. that the introduction of the inhibitor does not alter the structure of the metal compound and that the rate of consumption of the inhibitor is independent of its initial concentration).

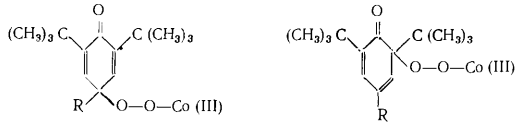
The occurrence of reaction (2) in the oxidation of α-methylstyrene in the presence of the copper complex of α-phthalocyanine has been postulated[20,21] on the grounds that the copper complex of α-phthalocyanine can be an active catalyst of the oxidation of α-methylstyrene, although it does not in

fact accelerate to any appreciable extent the degree of decomposition of the peroxide formed in this process.

Kinetic evidence for reaction (2) has been obtained in the study of the oxidation of styrene in the presence of cobalt stearate, which is also inactive in the decomposition of the polyperoxide formed.[22]

The complex of vitamin B_{12} and O_2 [a mononuclear paramagnetic cobalt(II) superoxo-complex[9]] can interact with hydroquinone and ascorbic acid to form free radicals from the substrate.[23]

Direct evidence for the occurrence of reaction (2) has been obtained by EPR in the oxidation of 2,6-di-t-butyl-4-R-phenols in the presence of bivalent cobalt complexes with Schiff bases (CoL_2).[24] It has been shown that the concentration of the superoxo-complexes, formed in the interaction of molecular oxygen with CoL_2 and detected by EPR, falls sharply when phenols are added to the solution. Under anaerobic conditions, one can then observe the formation of the corresponding free phenoxy-radicals. In an atmosphere of oxygen the reaction is not catalytic and leads to the formation of quinones:



with insertion of the Co(III)OO group in the *p*-position of the phenol for R = CH_3, C_2H_5, iso-C_3H_7, or t-C_4H_9 or in the *o*-position for R = $C_6H_{11}R'$. The phenoxy-radicals formed in the first stage of the process are apparently reduced by cobalt(II) ions with formation of the corresponding phenoxides, which react further with molecular oxygen at high rates.

The possibility of the involvement of the catalyst in the oxidation chain initiation stage, apparently owing to the preliminary formation of superoxo-complexes, has been demonstrated in relation to the oxidation of ethylbenzene in the presence of nickel bis(acetylacetonate).[25] The rate of chain initiation measured by the method of inhibitors proved to be 4×10^{-7} and 9×10^{-6} mol litre^{-1} s^{-1} in this process at 120 °C and catalyst concentrations of 3×10^{-3} and 2×10^{-2} M respectively. These rates are significantly higher than the rate of chain initiation in the absence of catalysts (1.5×10^{-9} mol litre^{-1} s^{-1}).[26]

Such high rates of formation of free radicals in the catalytic process could not be ensured by the decomposition of hydroperoxides, since nickel bis(acetylacetonate) exhibits only a weak activity in their decomposition reaction. In order to attain the above rates of formation of free radicals, the content of hydroperoxides in the system should have been not less than 0.01 M,[27] while the experimental concentration $[ROOH]_0$ in ethylbenzene at the beginning of the process did not exceed 1×10^{-4} M.

The addition of electron-donating ligands [alkali metal stearates,[28,29] dimethylformamide (DMF), hexamethylphosphoramide, or *N*-methyl-2-pyrrolidinone[30]], which form complexes with nickel bis(acetylacetonate), leads to an appreciable increase (by a factor up to 3) of the rate of formation of free radicals, although the rate of decomposition of hydroperoxides in the presence of electron-donating ligands diminishes.[28] As for the cobalt(II) complexes,[31,32] the coordination of electron-donating ligands apparently increases the equilibrium formation constant of the complex of molecular oxygen with the catalyst and lowers its oxidation-reduction potential, which creates in its turn more favourable conditions for reaction (2).

Free radicals are apparently formed in the interaction of RH_2 with metal superoxo-complexes in the oxidation of ethylbenzene in the presence of copper complexes of *o*-phenanthroline (*o*-phen).[33] The rate of absorption of oxygen (W_{O_2}) in this system depends greatly on the concentration of the dissolved oxygen and is described by the empirical equation

$$W_{O_2} = a(b + c[O_2])^{1/2},$$

where *a*, *b*, and *c* are constants.

The observed rate law agrees qualitatively with the following oxidation mechanism:

$$\mathrm{Cu(II)}(o\text{-phen})_n \xrightarrow{\mathrm{ROOH}} \mathrm{Cu(I)}\,(o\text{-phen})_n,$$

$$\mathrm{Cu(I)}\,(o\text{-phen})_n + O_2 \rightarrow \mathrm{Cu(II)}\,(o\text{ phen})_{n-1}O_2^{\cdot-} + (o\text{-phen}),$$

$$\mathrm{Cu(II)}\,(o\text{-phen})_{n-1}O_2^{\cdot-} + RH_2 \rightarrow HR^{\cdot} + HO_2^{\cdot} + \mathrm{Cu(I)}\,(o\text{ phen})_{n-1},$$

$$HR^{\cdot} + O_2 \rightarrow HRO_2^{\cdot},$$

$$HRO_2^{\cdot} + RH_2 \rightarrow HROOH + HR^{\cdot},$$

$$2HRO_2^{\cdot} \rightarrow \text{chain termination}.$$

The porphyrin complexes of nickel, iron, and manganese can also serve as initiators of the free-radical oxidation reaction.[34-36]

III. THE MONOXYGENASE OXIDATION MECHANISM

The monoxygenase oxidation mechanism is the term which has come to be given to the mechanisms of catalytic reactions with participation of molecular oxygen in which one oxygen atom is consumed in the oxidation of the substrate, while the other is reduced to water. The reaction takes place without the intermediate formation of free radicals in accordance with the overall equation

$$RH_2 + O_2 + DH_2 \rightarrow HROH + D + H_2O.$$

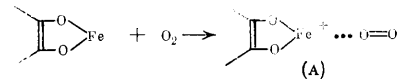
The enzymes catalysing such oxidation reactions have come to be called monoxygenases.

When a cofactor does not participate in the process, i.e. when the reaction proceeds in accordance with the overall equation

$$RH_2 + O_2 \rightarrow R{=}O + H_2O,$$

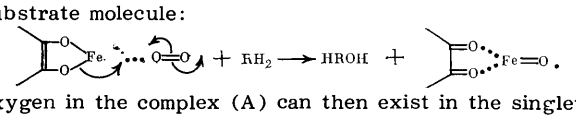
the monoxygenases of this type are referred to as internal monoxygenases.[37]

It has been suggested that in catalysis by monoxygenases oxygen is inserted in the substrate molecule via an intermediate stage involving the formation of oxenoid complexes (by analogy with carbenoid complexes), in which the oxygen atom has six electrons.[38] The hydroxylation of alkanes and aromatic compounds as well as the epoxidation of olefins can proceed via the oxenoid mechanism. For example, in the hydroxylation of substrates in the presence of iron compounds, electron transfer from iron to oxygen could give the intermediate complex (A)



(A)

resulting in the transfer of an oxygen atom with six electrons to a substrate molecule:



The oxygen in the complex (A) can then exist in the singlet form, which facilitates the reaction without the intermediate formation of radical products.

One of the chemical systems whereby it is possible to model the action of monoxygenases is apparently the hydroxylation of aromatic compounds by molecular oxygen in the presence of molybdenum hexacarbonyl $Mo(CO)_6$.[39,40] This reaction is accompanied by the formation in the first macrostage of the process of an arenemolybdenum tricarbonyl in accordance with the scheme

$$Mo(CO)_6 = Mo(CO)_5 + CO,$$
$$Mo(CO)_5 + ArH \rightarrow Mo(CO)_5(ArH),$$
$$(ArH)Mo(CO)_5 \rightleftarrows (ArH)Mo(CO)_4 + CO,$$
$$(ArH)Mo(CO)_4 \rightleftarrows (ArH)Mo(CO)_3 + CO.$$

The formation of the complex $(ArH(Mo(CO)_3$ can be detected by ultraviolet and infrared spectroscopy. The rate-limiting stage in this macrostage of the process is the dissociation of $Mo(CO)_6$ with elimination of one CO molecule, which has been confirmed by the weak dependence of the rate of oxidation on the substrate concentration.

The final reaction products (phenols or naphthols) are formed in the interaction of arenemolybdenum tricarbonyl with oxygen. The rate of this macrostage depends on the oxygen concentration. It has been suggested[39-41] that the rate-limiting stage in the oxidation of arenemolybdenum tricarbonyl is the formation of the intermediate complex $(ArH)Mo(O_2)(CO)_3$. The formation of a ternary complex, in which both reactants (O_2 and the substrate) are coordinated to a zerovalent molybdenum atom, facilitates the insertion of one oxygen atom in the molecule of the aromatic compound:

$$(ArH)Mo(O_2)(CO)_3 \rightarrow ArOH + Mo(O)(CO)_3 .$$

The molybdenum dioxo-complexes $O{=}\overset{\diagup\diagdown}{Mo}{=}O$ can also serve as effective catalysts of the oxidation of many organic substances via a non-radical mechanism.[42-46] Thus the complexes $MoO_2(S_2CNR_2)_2$ can catalyse the oxidation of trialkyl- and triphenyl-phosphines by molecular oxygen with formation of the corresponding oxides. In the absence of oxygen, the reaction is stoichiometric and leads to the formation of the inactive complex $Mo_2O_3(S_2CNR_2)_4$:

$$MoO_2(S_2CNR_2)_2 + PR_3 \rightarrow MoO(S_2CNR_2)_2 + R_3PO,$$
$$MoO_2(S_2CNR_2)_2 + MoO(S_2CNR_2)_2 \rightarrow Mo_2O_3(S_2CNR_2)_4 .$$

In the presence of oxygen, the oxidation of tertiary phosphines becomes catalytic owing to the regeneration of the dioxo-complex on interaction of oxygen with $Mo_2O_3 \cdot (S_2CNR_2)_4$:[47]

$$Mo_2O_3(S_2CNR_2)_4 + O_2 \rightarrow Mo_2O_3(O_2)(S_2CNR_2)_4,$$
$$Mo_2O_3(S_2CNR_2)_4 + Mo_2O_3(O_2)(S_2CNR_2)_4 \rightarrow 4MoO_2(S_2CNR_2)_2 .$$

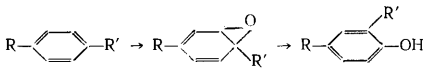
Reactions involving oxidation by molecular oxygen using cytochrome P-450 as the catalyst have attracted much attention because cytochrome P-450 forms part of the composition of microsomal oxidative systems.[37]

The cytochrome P-450 structure has been investigated by various methods and can now be regarded as fairly reliably established.[48-50] The iron atom in the complex is surrounded by four nitrogen atoms in equatorial positions; the axial ligands consist of cysteinyl sulphur and histidine.

It has been suggested that catalysis by porphyrins, metal complexes of azaporphyrins, and cytochrome P-450 ensures the development of the process via a non-radical pathway. In model systems cytochrome P-450 exhibits mainly a hydroxylating capacity, i.e. behaves similarly to monoxygenases, catalysing the incorporation of one oxygen atom in the substrate molecule.

Apart from the hydroxylation of aromatic and paraffinic hydrocarbons, the commonest reactions with participation of cytochrome P-450 as the catalyst involve the dealkylation of *S*-, *N*-, and *O*-substituted compounds.[37]

One of the most significant pieces of evidence showing that cytochrome P-450 catalyses the development of oxidative reactions via a non-radical mechanism is the high regioselectivity of such reactions, which is as a rule not characteristic of radical chain processes. As an example, one may point out that the hydroxylation of paraffinic hydrocarbons apparently proceeds with the preferential formation of 2-alkanols.[37] Examples of the oxygenation of substituted aromatic compounds, accompanied by a change in the position of the substituent in the aromatic ring, are known.[51] It has been suggested that the reaction proceeds via the intermediate formation of epoxides:



In the hydroxylation of aromatic compounds, the isomeric composition of the phenols formed is considered as one of the pieces of evidence for the molecular (monoxygenase) mechanism of the action of both cytochrome P-450 and other hydroxylating systems.

For many catalytic hydroxylating systems, incorporating iron(II), iron(III), copper(I), and titanium(III) ions as well as ligands with redox activity (the ascorbate ion, thiosalicylic acid, etc.), the proportions of the isomeric *ortho-para*-, and *meta*-phenols differ significantly from those of the corresponding isomers produced by the interaction of aromatic substrates with OH radicals.[52-56] This discrepancy can evidently be regarded as important evidence in support of the view that free hydroxy-radicals are not involved in the hydroxylation, but it cannot indicate unambiguously the interaction of the substrate with activated oxygen.

One of the important features of chemical hydroxylating systems is their ability to catalyse the epoxidation of olefins by molecular oxygen. Since this property is as a rule characteristic of enzymes (monoxygenases), it too can be regarded as evidence in support of a non-radical oxidation pathway.[57]

The hydroxylation of various substrates by molecular oxygen in the presence of cytochrome P-450 and NADPH(DH_2) is believed to proceed in several stages. A molecular complex of cytochrome P-450 with the substrate ($Fe^{3+}...RH_2$), which undergoes one-electron reduction on interaction with NADPH with formation of the $Fe^{2+}...RH_2$ species, combining with molecular oxygen, is formed in the first stage of the process. The ternary complex $RH_2...Fe^{2+}...O_2$ is reduced via a one-electron mechanism:

$$RH_2 \cdots Fe^{2+} \cdots O_2 \xrightarrow{\bar{e}} RH_2 \cdots Fe^{2+} \cdots O_2^- \rightleftarrows RH_2 \cdots Fe^{3+} \cdots O_2^{2-} .$$

The complex $RH_2...Fe^{3+}...O_2^{2-}$ contains iron in the formal +5 oxidation stage:[58]

$$Fe^{3+} \cdots O_2^{2-} \rightleftarrows Fe^{5+} \cdots O_2^{4-} .$$

This complex can be reduced via the oxenoid mechanism with the simultaneous transfer of two electrons to the oxygen molecule or via the peroxidase mechanism with the consecutive transfer of two electrons:[41]

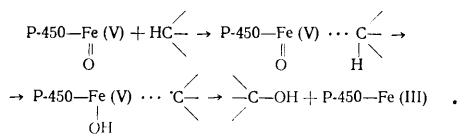
$$[Fe^{3+} \cdots O_2^{2-} \equiv Fe^{5+} \cdots O_2^{4-}] \xrightarrow{\bar{e}} [Fe^{3+} \cdots O_2^{3-} \equiv Fe^{4+} \cdots O_2^{4-}] \xrightarrow{\bar{e}} Fe^{3+}$$
$$\qquad\qquad\qquad

metal-O_2 complexes behave as hydroxylating agents only in aprotic media. In this case the transfer of an oxygen atom takes place via the oxenoid mechanism and the rate of the hydroxylation reaction is limited by the insertion of oxygen in the substrate molecule; in aqueous or other protic media, the hydroxylation takes place with participation of the free radicals OH or HO_2. An important element in the oxidation via the oxenoid mechanism in a ternary substrate–catalyst–oxygen complex is the activation of both reactants.[41]

The intermediate formation of radical species has been suggested also in the oxidation of norbornene in the presence of cytochrome P-450.[59] In this case oxidation by molecular oxygen leads to the formation of *exo*- and *endo*-2-norborneols in proportions of 3.4 : 1. The appreciable kinetic isotope effect (k_H/k_D = 11.5), found for this reaction, suggested[59] that the rate-limiting stage is the abstraction of a hydrogen atom from the norbornene molecule with the intermediate formation of an alkyl radical.

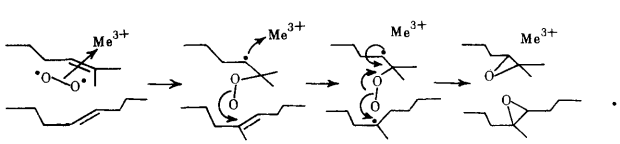
When oxygen interacts with cytochrome P-450, the oxo-complex P-450–Fe(V) of the formally quinquevalent iron is

formed in the first stage and then reacts with the hydrocarbon via the mechanism



In many investigations involving the use of metal-phthalocyanines as oxidation catalysts, the conclusion that oxygen can be activated by such complexes is based on the ability of metal-phthalocyanines to form complexes with oxygen.[60,61] However, the observed effects can be frequently attributed to the possibility of the formation of a catalyst–substrate complex and not the activation of oxygen. Thus the rates of oxidation of squalene and the composition of the products in the advanced process in the presence of cobalt-octaethylporphyrin, i.e. Co(OEP), and cobalt(III) and iron(III) tris(acetylacetonates), which cannot form complexes with molecular oxygen, are virtually identical.[62] Furthermore, it is known that there is an almost complete electron transfer in the molecular complexes of cobalt(II)-octaethylporphyrin with molecular oxygen to form a superoxide ion coordinated to a tervalent cobalt ion.[63] The interaction of this complex with an olefin should have led to the formation of the octaethylporphyrin complex of tervalent cobalt, which is incapable of coordinating oxygen, i.e. the oxidation in the presence of Co(OEP) should have been non-catalytic. Nevertheless, the number of substrate molecules reacting per catalyst molecule reaches 100.

The principal squalene oxidation products are epoxides; allyl alcohols and ketones, which are the main products of the oxidation of low-molecular-weight olefins, are virtually absent from the oxidation reaction mixture.[63] Since squalene is associated in solution[64] and a parallel arrangement of the chains is characteristic of the associated species, it has been suggested that the bimolecular interaction of the free-peroxy-radical with the double bond of a second squalene molecule plays an important role in the oxidation mechanism:



The dependence of the rate of oxidation W of pyridine solutions of ascorbic acid (H_2A) on the oxygen concentration in the presence of catalytic amounts of iron(III), copper(II),[65] UO_2^{2+},[66] VO_2^+,[67] and zinc(II)[68] complexes is described by the law

$$W = \frac{(k_1 + k_2[\mathrm{Py}])[\mathrm{HA}^-][\mathrm{O_2}][\mathrm{cat}]}{[\mathrm{H}^+](1 + K_a[\mathrm{HA}^-])},$$

This suggested[65–67] that the process proceeds via a non-radical mechanism as a result of the activation of molecular oxygen. It is evident, however, that an analogous dependence might have been obtained also for a radical non-chain mechanism[69] if it is assumed that the first stage of the process involves the formation of a molecular complex of the catalyst with the ascorbate anion HA^-, which dissociates in the coordination sphere of the catalyst with formation of the dianion A^{2-}. The oxidation of the coordinated dianion by molecular oxygen leads to the formation of the radical-anion $A^{\cdot-}$, which then disproportionates in the system. Indeed, it has been found that the $A^{\cdot-}$ concentration measured by EPR in the solution being oxidised is virtually identical with that calculated on the assumption of a radical non-chain oxidation mechanism.[69]

Among porphyrin complexes of both cobalt and iron, the highest activity in the oxidation reaction is shown by complexes having the composition M–P : O_2 = 1 : 1:

$$\mathrm{LCo{-}P} + \mathrm{O_2} \rightleftarrows \mathrm{LCo{-}P \cdots O_2}, \qquad (3)$$

where L is an axial ligand and P is a porphyrin.

The hydroxylating activity of the catalyst falls appreciably on dimerisation (disproportionation) of mononuclear complexes:

$$\mathrm{LCo{-}P \cdots O_2 + LCo{-}P \rightleftarrows LCo{-}P(O_2)P{-}CoL}. \qquad (4)$$

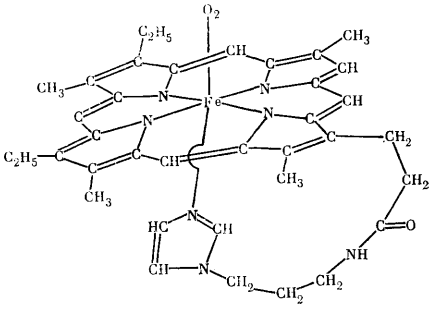
Depending on the reaction conditions, both mononuclear[70] and dinuclear,[71,72] complexes can be formed in solution. The formation of mononuclear 1 : 1 complexes with oxygen is characteristic of cobalt(II) complexes of protoporphyrin IX, while the irreversible reaction (4) takes place on raising the temperature.[73] It has been suggested that reaction (4) is preceded by a rearrangement of the complex LCo–P...O_2 in which the length of the O–O bond increases and its multiplicity diminishes.

The structure of the complex, in particular, the presence of a fairly strong base in the axial position, has a considerable influence on the complex-forming capacity of porphyrins in the reaction with molecular oxygen. In the complex formation reaction of Co(II)–P′ (where P′ is protoporphyrin IX) with oxygen, a satisfactory correlation is observed between the enthalpy of complex formation and the basicity of the axial ligand L[73] in the following sequence: benzimidazole < 4-t-butylpyridine < imidazole < 1-methylimidazole. The marked difference between the rate constants for reaction (4) with L = pyridine and imidazole suggested[73] that the stability of the oxygen complexes incorporating imidazole is ensured by the formation of hydrogen bonds between imidazole and O_2^- in the complex with the metal-porphyrin.

The presence of imidazole in the axial-position in haem-containing compounds has different effects on the rate constants for the complex formation reactions of haems with oxygen and carbon monoxide.[74,75] Thus the replacement of pyridine by imidazole hardly alters the rate constant for the formation of a complex of CO with mesohaem, while the corresponding rate constant for oxygen increases at least by a factor of 3.8×10^3.[76] In order to account for this effect, it has been suggested that the high π-basicity of imidazole plays a major role in the process. It strengthens the π-bond (compared with other bases) between iron ions and

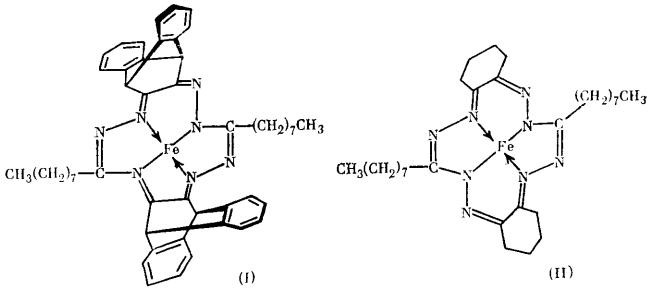
the unoccupied oxygen π* orbitals. The strength of the π-bond between iron and the A–B molecule (CO or O_2) should increase with increasing σ-basicity of the A–B molecule. Since the σ-basicity increases on passing from CO to O_2, the replacement of pyridine by imidazole should have a greater influence on the complex formation reaction of LCo–P with oxygen than with carbon monoxide.

The role of structural factors has been noted in a study of the stability of the complexes of O_2 with a synthetic section of the active centre of myoglobin:[77]



The possibility of the formation of this complex with molecular oxygen is also determined to a large extent by the presence of imidazole in the 5-position.

The influence of the structural factor on the complex formation reactions involving oxygen and also on the stability of oxygen complexes has been demonstrated.[78] The study of the interaction of O_2 with two complexes differing in the depth of the "cavity" formed by the ligand in which the iron atoms are located has shown that compound (I), in which the depth of the "cavity" is 5 Å, forms with oxygen reversible bright cherry-red 1:1 complexes. Compound (II), in which the depth of the "cavity" is 2.2 Å, combines irreversibly with oxygen in the stoichiometric proportions O_2:Fe = 0.5:1:



(I) (II)

The study of the mechanism of the oxidation of organic substances in the presence of rhodium(I) complexes has attracted much attention from the standpoint of the possibility of the activation of molecular oxygen. It has been suggested that the oxidation of olefins in the presence of chlorotris(triphenylphosphine)rhodium(I) takes place via the monoxygenase mechanism.[79–84] Triphenylphosphine, which is oxidised to the corresponding oxide under these conditions, functions as the reducing agent in the above process.

In one of the early studies of this cycle,[85] it was shown that chlorotris(triphenylphosphine)rhodium is an effective catalyst of the oxidation of aromatic compounds at temperatures above 100 °C.

An interesting feature of the process is the marked dependence of the rate of oxidation on the oxygen pressure,[85,86] which is not characteristic of catalytic oxidation via a radical chain degenerate branched mechanism. Such a dependence presupposes the involvement of oxygen in the rate-limiting stage of the reaction.

Although chlorotris(triphenylphosphine)rhodium and chlorocarbonylbis(triphenylphosphine)rhodium greatly accelerate the decomposition of hydroperoxides,[85,87] this does not rule out the possibility of the involvement of complexes of molecular oxygen with rhodium compounds both in the chain initiation stage [via reaction (2)] and in non-radical oxidation reactions of the substrates.

Lines due to the formation of species comprising rhodium(II) and O_2^-,[87,88] possibly the superoxo-complexes Rh(II).O_2^-, can be identified in the EPR spectra of solutions of $Rh(PPh_3)_2$. .COCl, saturated with oxygen, at 77 K. The concentration of these species increases greatly in the presence of cumenyl hydroperoxide,[87] apparently as the result of the facilitation of electron transfer from rhodium(I) to O_2 in the ternary complex:

$$ROOH \overset{\curvearrowright}{\cdots} Rh(I) \overset{\curvearrowright}{\cdots} O_2 .$$

The oxidation of cyclohexene by molecular oxygen in the presence of rhodium complexes activated by cumenyl hydroperoxide leads to the formation of cyclohexenyl hydroperoxide with a selectivity up to 95%.[86] Calculation of the rate of oxidation by the formula

$$W_{O_2} = (k_2/k_6^{1/2})[RH]W_i^{1/2} ,$$

where W_i is the rate of formation of free radicals in the decomposition of the hydroperoxide and k_2 and k_6 are respectively the rate constants for the oxidation chain propagation and termination, i.e. on the assumption of a radical chain oxidation mechanism, showed that the calculated W_{calc} is virtually identical with experimental W_{exp} only at the beginning of the process (at $t \to 0$); in later stages $W_{exp}/W_{calc} > 3$. This finding as well as the decrease of the reaction order with respect to the concentrations of cumenyl hydroperoxide (activator), the catalyst, the olefin, and oxygen from 1 to 0 as the concentration of the corresponding reactant increases suggested that the olefin is oxidised via a non-radical mechanism involving the formation of a ternary catalyst–substrate–oxygen complex after the preliminary modification of the catalyst in accordance with the scheme

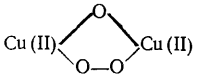
$$Rh(CO)Cl(PPh_3)_2 + ROOH \rightleftarrows Rh(CO)Cl(PPh_3)(ROOH) + PPh_3 ,$$
$$Rh(CO)Cl(PPh_3)(ROOH) + O_2 \rightleftarrows Rh(II)(CO)Cl(PPh_3)(ROOH)\cdot O_2^- ,$$
$$Rh(II)(CO)Cl(PPh_3)(ROOH)\cdot O_2^- + RH \rightarrow$$
$$\rightarrow Rh(II)(CO)Cl(PPh_3)(ROOH)\cdot O_2^-(RH) ,$$
$$Rh(II)(CO)Cl(PPh_3)(ROOH)\cdot O_2^-(RH) \rightarrow$$
$$\rightarrow ROOH + Rh(I)(CO)Cl(PPh_3)(ROOH) .$$

The catalyst in the initial form as well as rhodium(III) complexes and salts catalyse the radical chain oxidation pathway, which apparently explains the appearance of long induction periods after the introduction of different inhibitors at the beginning of the reaction in the presence of univalent rhodium compounds.[89] It is significant that the effectiveness of the modification of the catalyst by hydroperoxides depends greatly on the structure of the latter. For example, cyclohexenyl hydroperoxide hardly modifies the rhodium catalyst.[86]

The results of experiments using labelled oxygen must be regarded as the most reliable evidence in support of the mechanism involving the direct oxidation of substrates by molecular oxygen. With the aid of this method, combined with a series of kinetic methods, the possibility of the activation of molecular oxygen by high-spin complexes of bivalent nickel with a macrocyclic nitrogen-containing ligand has been demonstrated unambiguously.[90,91]

The hydroxylation of aromatic compounds, in particular cresols, in the presence of such complexes in an atmosphere of $^{17}O_2$ in solution in $H_2{}^{18}O$ showed that the phenol formed contains a ^{17}O atom, i.e. that oxygen is inserted in the direct interaction between ArH and O_2.

The possibility of the effective utilisation of a series of dimeric univalent copper complexes as models of monoxygenases has been demonstrated in recent years.[92–95] The formation of the dinuclear peroxo-complexes



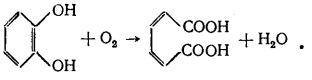
plays an important role in the mechanism of the activation of oxygen by such complexes.[96]

IV. MODELS OF THE ACTION OF DIOXYGENASES

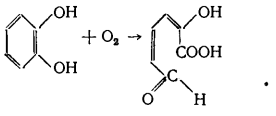
Enzyme systems catalysing the insertion of both atoms of molecular oxygen in the molecule of the substrate being oxidised (S) have come to be called dioxygenases. As a rule, such reactions do not require the participation of an extermal reductant in the process and are formally described by the equation

$$S + O_2 \rightarrow SO_2 .$$

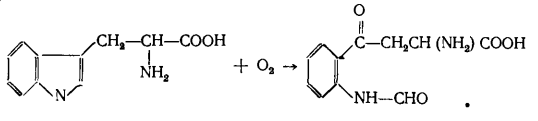
The most typical dioxygenases are catechol dioxygenases, protocatechuate dioxygenases, and tryptophan oxidases. The active centre in catechol 1,2-dioxygenase and protocatechuate 2,3-dioxygenase is a high-spin Fe^{3+} ion.[97–99] In the presence of these enzymes, the oxidation reaction proceeds with the dissociation of a C–C bond and, for example, in the oxidation of catechol leads to the formation of muconic acids:[100]



The metapyrocatechases—catechol 2,3-dioxygenases and protocatechuate 4,5-dioxygenases—contain iron in the form of Fe^{2+} and catalyse the *meta*-cleavage of catechols:[101]



Tryptophan 2,3-dioxygenase, whose composition includes the Cu^+ ion, catalyses the oxidative cleavage of the indole ring in tryptophan:[102]



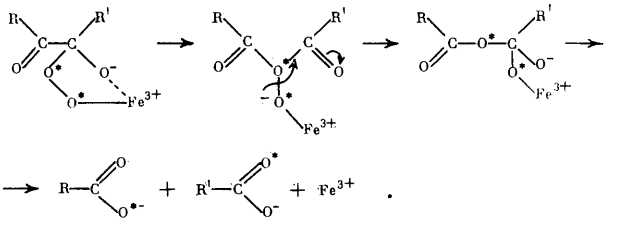
The mechanism of the action of all three enzyme systems involves many different intermediate stages, associated, in particular, with the rearrangement of the enzyme–substrate complexes formed initially.

The mechanism of the action of catechol 1,2-dioxygenases has been studied in greatest detail.[100,103,104] Experiments with $^{18}O_2$ have shown[100,103] that, in the course of the oxidation of catechols in the presence of catechol 1,2-dioxygenase, both atoms of molecular oxygen are incorporated in the oxidation product and no isotope exchange with the medium is observed. The reaction is accompanied by the formation in the first stage of an enzyme–substrate complex, which reacts further with molecular oxygen:[100,104]

$$E + S \rightleftarrows ES + O_2 \rightleftarrows ESO_2 \rightarrow ESO_2^* \rightarrow EP \rightleftarrows E + P,$$

where E is the enzyme, S the substrate, and P the reaction product.

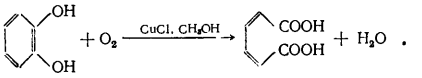
In certain cases, the formation of a "primary" complex with oxygen (ESO_2) may be detected in the system. However, in most systems the complex ESO_2 rapidly rearranges to form the "secondary" oxygen complex (ESO_2^*), and the rate of reaction is so high that the formation of the "primary" complex cannot be detected even by the stopped flow method and its formation can be inferred only indirectly on the basis of kinetic data.[100] The structures of the complexes ESO_2 and ESO_2^* have not been established. However, it is known that the formation of the intermediate complex ESO_2^* and its decomposition are accelerated when electron-donating substituents are introduced in the *para*-position in the benzene rings of catechols. This and also the finding that there is no change in the valence [oxidation state] of iron during the oxidation of catechols suggested that the reaction product is formed as a result of the insertion of oxygen in the C–C bond and is accompanied by the migration of an acyl group:



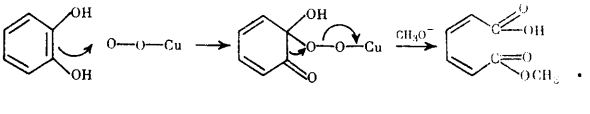
In the above formula the astericks denote the atoms of molecular oxygen.

Very few chemical models of the action of dioxygenases, in which the dioxygenase mechanism of the oxidation by molecular oxygen is demonstrated, have been described in the literature and as a rule the evidence presented cannot be regarded as unambiguous.

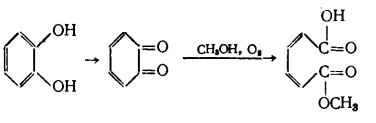
Copper(I) chloride catalyses the oxidation of catechol to muconic acid by oxygen in methanol in the presence of amines:[105]



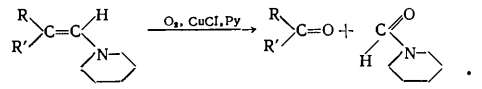
Although formally this reaction can be regarded as a model of the action of catechol 1,2-dioxygenase, in reality experiments with $^{18}O_2$ have shown that only one atom of the oxygen molecule enters into the composition of muconic acid.[105] The reaction can proceed via the intermediate formation of a peroxo-complex.[105] Its product is formed as a result of the interaction of the peroxo-complex with the anion CH_3O^-:



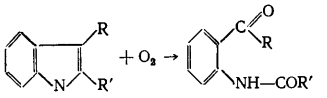
It has been suggested[106] that muconic acid is formed in the consecutive reaction



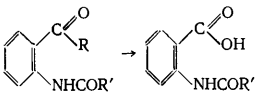
In pyridine solutions copper(I) chloride catalyses the oxidation of various substrates by molecular oxygen[107–109] at room temperature. For example, enamines are oxygenated with cleavage of the double bond and the formation of a ketone and *N*-formylpiperidine:[107]



The CuCl + amine system can serve as an effective catalyst of the oxidation of tryptophan and substituted indoles[108] at 25 °C. The reaction is accompanied by the dissociation of the double bond:



This system can be regarded as a model of tryptophan 2,3-dioxygenase which is capable, as pointed out above, of catalysing the oxidation of tryptophan [R = $CH_2CH(NH_2)$.COOH, R' = H]. However, formylkynurenine, which is a product of the enzymic oxidation of tryptophan, accumulates in the model chemical system in very small amounts (up to 1%) owing to its instability in relation to oxygen in the presence of pyridine complexes of univalent copper. The carbonyl compounds formed initially are oxidised at high rates and with a selectivity up to 60% to 2-acetamidobenzoic acid:[108]

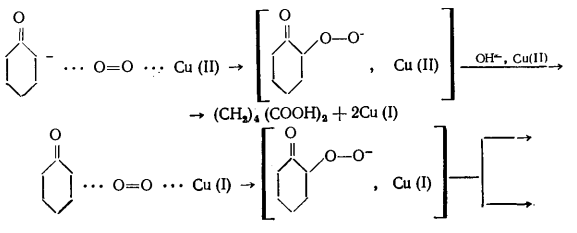


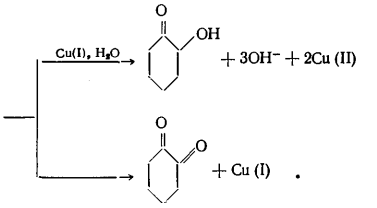
Thus the chemical system is less selective. The dinuclear μ-peroxo-complex Cu...O_2...Cu apparently serves as the oxygen transferring agent in the CuCl + O_2 + pyridine system.[110,111] The role of pyridine reduces to increasing the degree of dissociation of the dimeric form of copper(I) chloride $(CuCl)_2$, which is inactive in the reaction with molecular oxygen.

Certain cobalt complexes with Schiff bases[112] and with porphyrins[113] can also be regarded as models of tryptophan 2,3-dioxygenase.

The oxidation of alcohols and ketones in alkaline solutions in the presence of copper(II) complexes of *o*-phenanthroline can apparently also proceed via the dioxygenase mechanism.[33,114,115] The rate of oxidation of ketones in such a system increases linearly with increasing alkalinity of the medium,[116,117] i.e. as in the enzymic oxidation of catechols;[118] the deprotonation of the substrate plays a significant role in this process.

The reaction takes place via a non-radical mechanism, as shown, in particular, by the sequence in the formation of the reaction products, which is unusual for a radical-chain oxidation reaction: in the initial stages of the oxidation of cyclohexanone, the only oxidation products are adipic acid and cyclohexane-1,2-dione.[117] The latter is oxidised at rates much lower than the rate of accumulation of adipic acid, so that both products are formed via parallel (in relation to the substrate oxidised) pathways:





The rate of oxidation of ketones and the process selectivity (reaching 90–95% in the presence of *o*-phenanthroline) decrease greatly when 5-nitro-1,10-phenanthroline is used as the ligand,[116] which makes it possible to regard the reaction

$$RO^- + Cu(II)L_2 \rightarrow RO^{\cdot} + Cu(I)L_2 ,$$

whose rate should increase on passing from *o*-phenanthroline to 5-nitro-1,10-phenanthroline, as insignificant.

The increase of the rate of formation of free radicals when cyclohexane-1,2-dione is introduced at the beginning of the reaction also reduces the rate and selectivity of the oxidation of ketones.

The hypothesis of the involvement of superoxide ions in the process[114] is also inconsistent with experiment, since it is known that the complex $Cu(o\text{-phen})_2$ can play the role of superoxide dismutase[119] and the O_2 [O_2^-?] concentration in solution should therefore be negligible. Furthermore, the superoxide ion can react rapidly with *o*-phenanthroline,[120] which should have led to its consumption during the oxidation process. Nevertheless the concentration of *o*-phenanthroline hardly changes in the oxidation of ketones.

Thus the $CuCl_2$ + *o*-phenanthroline + base catalytic system can be regarded as one of the systems in which the simultaneous activation of both oxygen and the substrate by the catalyst leads to the operation of a non-radical oxidation mechanism, ensuring a high process selectivity close to room temperature.

The examples quoted above demonstrate the practical feasibility of liquid-phase oxidation processes at high rates and with high selectivities via a non-radical mechanism at comparatively low temperatures (close to room temperature) using as catalysts relatively simple catalytic systems modelling the action of biological enzymes.

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Diffusion and Sorption of Aqueous Electrolyte Solutions in Polymers

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The diffusion and solubility of electrolytes in polymers of different types (hydrophobic, hydrophilic, and moderately swelling) are examined. Diffusional transport in such systems is characterised by a number of features: dissociation, ion hydration, the formation of water clusters, and interaction with the functional groups of the polymer. The concentration dependence of the diffusion coefficients is analysed taking into account these effects and also the influence of the volume fraction of the polymer on the diffusion parameters. The mechanism of the distribution of the electrolyte in the hydrophobic and hydrophilic matrices is examined; it is shown that in the latter case account must be taken of the electrostatic factor, which influences the solubility of ions in polymers with ionogenic groups.
The bibliography includes 60 references.

CONTENTS

I. Introduction 885
II. Diffusion in hydrophilic polymers 886
III. Diffusion in moderately hydrophilic polymers 891
IV. Diffusion in hydrophobic polymers 893

I. INTRODUCTION

The investigations by Academician N.M.Emanuel' and his school on the degradation and stabilisation of polymers have led to the establishment of an independent and important field of chemical science dealing with such topics. It concerns the study of the structure and morphological changes in polymers as well as rational methods for controlling and regulating these changes.[1,2] When polymeric materials come into contact with liquid corrosive media, hydrolytic degradation takes place involving the diffusion of the components of the corrosive medium (acids, bases, salts, and water). In many cases of practical importance the rate of diffusional transport determines the limiting conditions under which polymers can be used. For example, the required properties of anticorrosion coatings in petroleum and gas mains include low diffusion coefficients in them of atmospheric and soil moisture as well as electrolytes; the polymer coating can then be used for a long time. On the other hand, self-degrading coatings of medicinal drugs or dialysis membranes should possess effective transport characteristics, which permit a productive and controllable liberation of medicinal drugs or separation of components.

The mechanism of diffusional transport in aqueous electrolyte solutions in a polymer is determined to a significant extent by the strength of the interaction between water molecules and macromolecules.[3] The subdivision of polymers into hydrophobic, hydrophilic, and moderately hydrophilic, proposed by Reitlinger,[4] therefore appears quite natural. Although the classification of hydrated polymer systems known at the present time as hydrophobic (in which the equilibrium water content under normal conditions and for 100% humidity is not more than 1%), hydrophilic (containing more than 10% water under the same conditions), and moderately hydrophilic (with an intermediate water content) simplifies the overall picture of the interaction of polymers with water, nevertheless it is also convenient from the practical point of view. In considering the diffusion of electrolytes, we shall adhere to this classification. We shall only note that the arbitrary nature of such subdivision arises from the dependence of the strength of the interaction of the macromolecules with water on temperature and from the variation of the degree of crystallinity of the polymer (recrystallisation, conversion into an amorphous form).[5]

The degree of hydrophilicity, i.e. the content of the water which has undergone equilibrium dissolution in the bulk of the polymer, can be estimated quantitatively with the aid of the solubility parameter δ ($J^{1/2}$ $m^{-3/2}$) [6] using the method of group contributions[7] and the Flory–Huggins theory of polymer solutions.[8]

Information about the overall content of water in the polymer is of limited value for measurements of the rate of diffusion, because the same amount of water can exist either in the bound state in the vicinity of polar groups of the macromolecules or can be distributed freely in the hydrophobic region. The mobilities of water molecules in the bound and free states are different.[9] The most reliable information about the transport mechanism is provided by the combined use of diffusion measurements and spectroscopic and relaxation methods. It is then possible to record not only the rate at which the electrolyte enters the polymer but also the structural changes accompanying diffusion.[10]

On the basis of extensive experimental data, one can assume that the first water molecules sorbed by the hydrophobic polymer are distributed between the units of the non-polar chain and that the energetic contribution of this process to the free energy of absorption is extremely low. A further increase in the moisture content in the system entails the preferential interaction between the water molecules and the consequent formation of clusters. This effect appreciably diminishes the mobility of water molecules, which is characterised by a decrease in the diffusion coefficients with increasing water concentration in the polymer.

Another situation arises in the diffusion of water in hydrophilic polymers. Here water molecules initially interact strongly with the highly polar groups of the polymer—the ionic and polar fragments are hydrated. The subsequent portions of water plasticise the polymer matrix, which leads, firstly, to an increase of the mobility of the segments (the polymer passes from the vitreous to the highly plastic state) and, secondly, to an increase in the fraction of "free" non-hydrating water in the polymer. Many hydrophilic polymers can undergo a transition under normal conditions into a viscous fluid state and they combine fully with water to form solutions provided that they are not cross-linked [poly(vinyl alcohol)(PVA), proteins]. Weakly cross-linked hydrophilic polymers can undergo limited swelling and their water content can reach several hundreds. The morphology

(porosity, crystallinity) of the hydrophilic polymers then changes significantly. A number of characteristic features of the diffusion of water in strongly swollen gels make it similar to the diffusion of water in solutions.

Moderately hydrophilic polymers combine with water to a limiting extent at room temperature even when they are in an amorphous state and are not cross-linked. They are also capable of the transition from the vitreous to the highly elastic state (for example, in the case of polyamides), of undergoing a change in the degree of crystallinity, and also of undergoing a change in the type of crystal lattice and pore deformation.[11] More refined effects, for example a transition from one crystalline modification to another (cellulose)[11] or the establishment of the liquid crystal state,[5] are also possible. When the transport of water is considered under conditions where the water content in polymers undergoing limited swelling is low, it is necessary to take into account the superposition of two transport mechanisms: one of them is analogous to diffusion in a hydrophilic polymer when the diffusing substance is in the vicinity of the polar group, while the other resembles diffusion in hydrophobic polymers when the water molecule overcomes hydrophobic regions whose dimensions significantly exceed the length of the diffusional jump. When the moisture content of the specimen is high, account must be taken of extensive hydrated regions where the macromolecules have been plasticised and the transport model should not differ greatly from the transport model in hydrophilic polymers.

II. DIFFUSION IN HYDROPHILIC POLYMERS

The multiplicity of phenomena accompanying the diffusion of electrolyte solutions in polymers can be characterised by the set of pair interactions presented in Table 1.[3] The predominance of a particular type of interaction depends on the nature of the polymer. For example, the diffusion in hydrophobic polyolefins and polysiloxanes is complicated by interactions of the water–water (cluster formation) and water–electrolyte type,[12] while in polar polymers the interaction of the polymer–electrolyte type becomes dominant.[13]

Electrolytes alter the physical structure of the polymer either by direct interaction with various polar and ionised groups or indirectly as a result of the influence of the ions on the structure and activity of the solvent. The direct interaction of ions with macromolecules can be both non-specific, i.e. can be determined by long-range Coulombic forces, and specific, being determined by the specific influence which the electrolyte exerts on the conformation of the macromolecules, for example, in its competition with water for the formation of hydrogen bonds with the functional groups of the polymer (guanidinium salts, hydrochloric and hydrofluoric acids) or in the course of the redistribution of hydrophobic contacts (tetra-alkylammonium ions) in the polymer.[14]

1. Relation between the Diffusion Coefficients and the Volume Content of the Polymer

It is useful to begin the examination of the diffusion of electrolytes in polymers in terms of the somewhat simplified but frequently employed Mecke-Meares and Yasuda theories (see, for example, Moiseev and Zaikov[15] p.119). The essential features of these theories consist in the attempt to relate the diffusional parameters of the solutes (the diffusion coefficient D and the permeability P) in hydrophobic polymers containing different amounts of water to the diffusion coefficient of the electrolyte in the pure solvent (D^0). On the basis of the above theories, it becomes possible to predict the diffusion coefficients of the electrolyte in the polymer D knowing only D^0 (tabulated data) and the volume concentration of water in the polymer ϕ_w (experimental data). Both theories treat the electrolytes as an individual substance; the effects of the ion–ion interaction, the deviations from ideality, and the possibility of partial dissociation are neglected.

Table 1. The types of interactions in electrolyte–water–polymer systems.[13]

Type of interaction	Nature of interaction	Manifestation at physicochemical level
Polymer–polymer	Electrical, polar, and dispersion interactions	Wide variety of ordered crystalline and supermolecular structures, the presence of three main physical states of the polymers (vitreous, highly elastic, and viscofluid)
Electrolyte–electrolyte	Electrical forces (ion–ion); ion–dipole interactions (for incompletely dissociated electrolyte molecules); hydrophobic interactions (for large organic ions)	The operation of Coulomb's law, the existence of an ionic atmosphere, dissociation, complex formation, etc.
Water–water	Dipole–dipole interactions	The existence of hydrogen bonds, the formation of ordered structures (clusters), cluster water–monomeric (free) water equilibrium
Electrolyte–water	Ion–dipole interactions	Hydration, formation of crystalline hydrates
Water–polymer	Polar and hydrophobic interactions	The hydration of polymer groups and segments, plasticisation, antiplasticisation, conformational transitions, crystallisation, transformations of crystal structures, conversion into an amorphous form, degradation, etc.
Electrolyte–polymer	Electrical and polar interactions, hydrophobic interactions (for large organic ions)	Conformational changes in macromolecules, change in crystal structure, complex formation, structure formation (by polyvalent ions), plasticisation

The Mecke-Meares theory of steric hindrance explains the decrease of the self-diffusion coefficients of electrolytes in hydrophilic polymers compared with aqueous solutions by the increase of the diffusional path, because the ions have to move round the macromolecules. In the absence of interaction between the functional polar groups of the polymer and the electrolyte, the polymer hindrance effect is taken into account by the factor

$$(1-\varphi_p)^2/(1+\varphi_p)^2,$$

where ϕ_p is the volume fraction of the polymer.

In contrast to the previous theory, Yasuda's theory uses the concept of the free volume instead of the mechanistic ideas about the polymer as a medium interfering with the movement of ions.[16] The hydrated polymer is regarded as a quasi-homogeneous matrix in which segmental movement of the macromolecules and the presence of the solvent result in the existence of an additive free volume

$$f_v = f_v^w \varphi_w + f_v^p \varphi_p, \qquad (1)$$

where ϕ_w and ϕ_p are the volume fractions and f_V^w and f_V^p are the free volumes of water and the polymer respectively. In formulating the expression for the diffusion coefficient of the electrolyte as a function of ϕ_w, the following assumptions

are made: (1) the effective free volume, in which the solute (electrolyte) is accommodated, corresponds to the free volume of water in the polymer, i.e. account is taken only of the first term of Eqn.(1); (2) the size of the fluctuating cavities, which determine the free volume, corresponds to the size of the diffusing species; (3) there is virtually no interaction between the polymer and the solute molecules.

The probability of the formation of a cavity whose dimensions correspond to the cross-sectional area of the diffusing species (S_S) is defined as $\exp(-BS_S/f_V)$, where B is a constant, for small electrolyte species. In this case the diffusion coefficient of the electrolyte in the polymer, where the volume fraction of water is ϕ_w, is defined by the equation

$$D = D^0 e^{-k_f(1-\Phi_w)\Phi_w^{-1}}, \qquad (2)$$

where $k_f = BS_S/f_V^w$.

It follows from Eqn.(2) that the diffusion coefficient D increases with increasing concentration of water in a hydrophobic polymer, approaching in the limit the diffusion coefficient of the electrolyte in pure water, which has been confirmed in a series of experiments. With decrease of the water content in the specimen, the diffusion coefficient of the electrolyte also falls. The shielding effect of water becomes weaker, so that the possibility of the direct interaction of the electrolyte ions with the macromolecules increases and Eqn.(2) ceases to hold for sufficiently low values of ϕ_w. It is therefore important to emphasise that, from the standpoint of the model considered, the polymer influences the diffusion of the electrolyte only indirectly by reducing the fraction of the free volume of water in the system.

Two important corollaries follow from Eqn.(2). Firstly, the dependence of $\lg D$ on ϕ_w^{-1} is more pronounced the greater the cross-sectional area of the diffusing species. Secondly, for a series of species of different cross-section and within a specific range of values of ϕ_w, the quantity $\lg(D/D^0)$ should decrease linearly with increasing S_S and the higher the water content in the polymer the more marked should be this dependence. To illustrate this conclusion, we shall resort to the results of a study[17] in which the above dependence was observed for a series of organic compounds diffusing in poly(hydroxyethyl methacrylate) hydrogels (Fig.1). The introduction of a cross-linking agent diminishes the water content in the polymer and, as follows from Eqn.(2), leads to a sharper decrease of the diffusion coefficient with increasing r^2, where r is the radius of the diffusing molecule.

Yasuda's model does not take into account the specific features of the electrolyte as a substance capable of dissociating into ions and it is therefore applicable mainly to natural solutes and does not describe the diffusion in polymers containing charged ionogenic groups (ion-exchange resins, polyelectrolytes).[18]

2. The Influence of the Ionogenic Groups of the Polymer on the Diffusion of Electrolytes

The question of the influence of the ionogenic groups of the polymer is important for understanding the mechanism of the processes involving the dyeing and hydrolytic degradation of synthetic and natural fibres, mainly polyamides; the influence of the charged groups on the transport of electrolytes in these polymers, which belong to an intermediate class, will be examined in greater detail in the next Section.

Nikolaev and co-workers[19,20] have made a considerable contribution to the development of ideas about the mechanism of the diffusion of electrolytes in ion-exchange resins. Ion-exchange resins as a rule contain large amounts of water and can be formally classified as hydrophilic polymers. In order to explain the diffusion in hydrophilic polymers containing ion-exchange groups, a loose quasi-crystal model has been proposed.[19] It is based on the following postulates: (1) owing to thermal movement, the counterions can move away from the functional group of the polymer and can give rise to defects resembling those in ionic crystals (vacancies and incorporated ions); (2) migration in the membrane takes place in two stages: during a period τ_0, the counterion is in a potential well, whose existence is due to the presence of the functional group, and oscillates about the equilibrium position. After that, during a period τ_1, it diffuses in a medium analogous to an electrolyte solution until it reaches the next functional group; (3) the functional groups are uniformly distributed in the polymer and in the swollen state the system is quasi-homogeneous.[20]

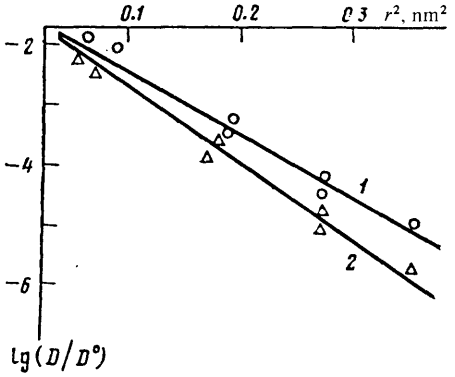

Figure 1. The influence of the size of the diffusing species on the diffusion coefficients in poly(hydroxyethyl methacrylate): 1) $\phi_w = 0.42$; 2) $\phi_w = 0.37$.[17]

The diffusion coefficient of the counterion in the polymer is determined by the two characteristic times τ_0 and τ_1:

$$D_i = \lambda^2/[6(\tau_0 + \tau_1)]^{-1}, \qquad (3)$$

where λ is the average distance between the nearest ionogenic groups, which is calculated on the basis of a scheme assuming the closest packing with the aid of the formula $6.6 \times 10^{-9} C_p^{-1/3}$ (C_p is the capacity of the swollen material, equiv.m^3). After the introduction of the tortuosity coefficient of the diffusion path (r_0) the final expression for the effective diffusion coefficient of an ion in the polymer is

$$D_i = D_i^0 r_0/[(\tau_0/\tau_1) + 1], \qquad (4)$$

where D_i^0 is the diffusion coefficient of the ion in solution.

Experimental measurements of the rate of diffusion in ion-exchange materials of different chemical nature indicate the possibility of the variation of D_i by 5–7 orders of magnitude, while the diffusion coefficients of ions in aqueous solutions vary only within the limits of one order of magnitude. Analysis of experimental results enabled the author to conclude that the main parameter determining the rate of diffusion in polymers is the residence time of the counterion in the vicinity of a given functional group. The stronger the bond between the counterion and the functional group, the longer the time τ_0 and hence the lower the diffusion coefficient.

A decrease in the water content of ion-exchange membranes, for example, as a result of the increase of the degree of cross-linking, strengthens the bond between the counterion and the functional group as a consequence of the diminution of the degree of their hydration. The decrease in the dielectric constant in the system when electrolytes diffuse from non-aqueous solvents also has a negative influence on the ionic mobility. For example, comparison of the diffusion coefficients of the Na^+ and Cs^+ ions in a Nafion membrane from aqueous solutions and acetonitrile ($\varepsilon = 37.5$) solutions showed that the diffusion parameters diminish in the less polar medium approximately by a factor of 120 for Na^+ and 550 for Cs^+.[21]

The presence of dissociating groups in the polymer complicates the electrolyte diffusion process as a result of the occurrence of ion-exchange reactions. The appearance of maxima on the kinetic curves for the sorption of electrolytes by polymers, which are absent in experiments with pure water, characterises the different capacities of the dissociating SO_3H and $SO_3^-M^+$ groups for the sorption of water (M^+ is a metal cation which can give rise to a neutral form).[22]

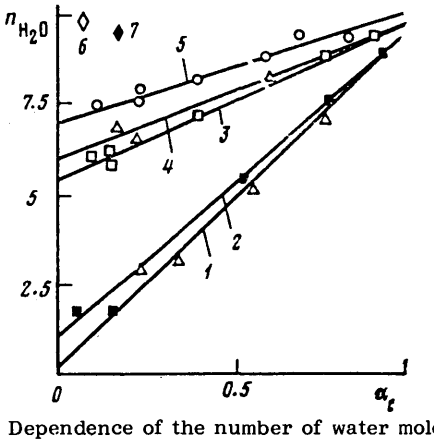

Figure 2. Dependence of the number of water molecules sorbed on the counterions of a "Nafion" membrane on the degree of substitution of the proton by the cation of the SO_3H group: 1) K^+; 2) Cs^+; 3) Ba^{2+}; 4) Sr^{2+}; 5) Ca^{2+}; 6) Al^{3+}; 7) Fe^{3+}.[22]

During the diffusion of a solution of alkali into a polymer specimen containing strongly acid groups, the latter are neutralised. At each instant, the following equation holds:

$$n_w = n_h(1-\alpha_c) + \alpha_c n_k = (n_h - n_k)(1-\alpha_c) + n_k, \qquad (5)$$

where n_h, n_k, and n_w are the numbers of moles of water sorbed by one mole of the acid and the neutral form of the sulpho-groups and the number of moles of water sorbed per mole of the counterion respectively and α_c is the degree of substitution of the proton in the SO_3H group by the cation.

In conformity with this equation, there is a linear relation between n_w for SO_3H and $1 - \alpha_c$. Fig.2 shows that the total amount of sorbed water per sulpho-group in the neutral form increases with increasing charge of the counterion in the sequence $K^+ < Cs^+ < Ba^{2+} < Sr^{2+} < Ca^{2+} < Fe^{3+} \cong Al^{3+}$, which can be explained by the polarising influence of the ion on the nearest water molecules. The diffusion kinetics of ion exchange are described in greater detail in a monograph.[23]

3. The Influence of the Chemical Structure of the Polymer on Diffusion

The term "chemical structure of the polymer" is understood as the chemical composition, the sequence of elementary units, and the degree of branching of the polymer chain. The principal characteristics of the chemical structure are the polarity of the macromolecule, steric factors (i.e. the stereoregularity of the macromolecule), and the ability of the molecules to form hydrogen, polar, and van der Waals linkages. There are important reasons to believe that the chemical structure determines the possibility of the existence of a structural hierarchy of polymers: the presence of α- and β-helices, crystallinity, supermolecular formations, porosity, etc. The possibility of obtaining a polymeric particle (membrane, coating, etc.) with the necessary degree of crystallinity or porosity depends on specific conditions in the preparation and previous history of the specimen: the choice of the solvent, the rate of its evaporation, the existence of temperature gradients, the character of the support, the storage conditions, and a number of others.[24,25]

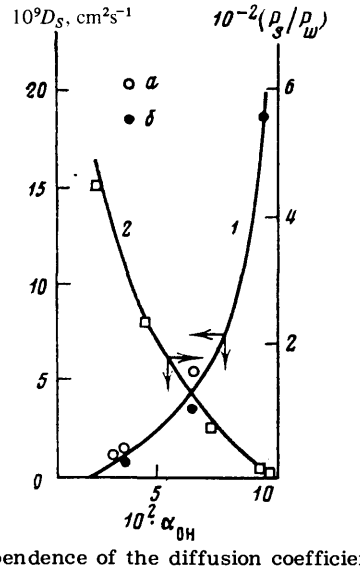

Figure 3. Dependence of the diffusion coefficients of NaCl (curve *1*) and of the relative permeability to the salt and water (curve *2*) on the weight fraction of the hydroxy-groups in cellulose acetate: *a*) stationary measurements; *b*) measurements of the delay time.[3]

As in the transport of water molecules, the permeability to and diffusion of electrolytes are regulated by the ratio of the hydrophilic and hydrophobic units of the macromolecules. Fig.3 presents the diffusion coefficients and the relative permeabilities for a salt and water (P_{NaCl}/P_W) in cellulose acetate films. Evidently, with increase of the weight fraction of hydroxy-groups, i.e. with decrease of the degree of acetylation, a sharp increase of the rate of diffusion of sodium chloride is observed. The principal cause of the increase of P_{NaCl} is the increased water content in the more hydrophilic matrix, which entails the plasticisation of the macromolecules and hence an increase in the free volume in the system.

The accompanying decrease of the relative permeability shows that, despite the overall tendency towards an increase of P_{NaCl}, the value of P_w under the conditions of an applied hydrostatic pressure increases faster, since the mechanism of water transport in strongly swelling membranes changes from diffusional to convective.[26]

A large difference between the mechanisms of the permeability of cellulose and nitrocellulose membranes has been demonstrated.[27] Since the conformations of the molecules of the modified and unmodified celluloses are virtually identical according to infrared spectrscopic data, the above differences can be caused only by the interaction of the OH and NO_2 groups with the solvent and solute and also by some increase in the size of the cavities accompanying the replacement of the nitro-groups in nitrocellulose by hydroxy-groups.

Interesting studies of the influence of the ratio of hydrophilic and hydrophobic units in the macromolecule have been made using membranes based on poly(ethylene terephthalate)-poly(hydroxyethylene glycol) (hydrophilic component) block-copolymers. Membranes of this type are used in medicine for the purification of blood plasma by removing low-molecular-weight impurities, salts, and urea. The linear dependence of the purification half-life on the content of the hydrophilic component in the matrix indicates the need to take into account the ratio of the hydrophilic and hydrophobic groups in the polymer in the solution of practically important problems in membrane separation. An increase of the content of poly(hydroxyethylene glycol) in the copolymer increases the degree of its swelling, which impairs, in its turn, the selectivity and mechanical properties of the film used for dialysis. In constructing separators, oxygenators, dialysis apparatus, etc., it is therefore necessary to select optimum conditions which ensure a high productivity of the membrane and reliable operating qualities of the given article. The hydrophobic blocks play an important role in the fulfillment of the latter requirement. By crystallising and forming domains, they protect the hydrophilic matrix from extensive swelling or dissolution, forming, as it were, effective cross-links.[25]

Membranes based on ethylene–potassium acrylate (25%) copolymers are used in silver-zinc accumulators. When styrene is grafted to the copolymer, the resistance of the polymer matrix to oxidative degradation in the electrolyte improves. It has been shown by an isotopic method that the permeability of membranes to OH^- ions passes through a maximum corresponding to a grafted styrene content of 2.5%, whereas a further increase of the hydrophobic component entails a decrease of P_{OH^-}, as was to be expected. The permeability to Ag^+ ions under the same conditions diminishes monotonically and, in the presence of 16.5% of styrene, the membrane becomes impermeable to Ag^+ ions.[28] These data as well as the results of a number of other studies show that specific conclusions about the influence of the hydrophilic-hydrophobic balance must be made to take into account the specific nature of the diffusing ion. In the example described above the hydroxide ion, as well as the H^+ ion, is characterised by an anomalous diffusional behaviour not only in solution but apparently also in many polymer systems capable of forming hydrogen bonds.

4. The State of the Electrolyte in the Polymer

(a) Ion hydration. The theory of the diffusion of electrolytes in polymers deals with hydrated species and ions as independent kinetic units and does not take into account quantitatively the exchange between the free water and the water of hydration, i.e. the dynamic character of hydration. The polymer matrix is regarded as an inert medium, usually quasi-homogeneous, in which there is sufficient water to ensure, firstly, the hydrolytic dissociation of the electrolyte and, secondly, that the ionic and functional groups of the macromolecules are in a hydrated state.

The commonest evidence for the presence of a hydration shell around the ions diffusing in a hydrophilic polymer is the observation that the sequence in which their diffusion coefficients vary is the same as for their diffusion coefficients in solution. The decrease of the diffusion coefficients of singly charged and multicharged ions in hydrophilic and weakly cross-linked polymer membranes corresponds to an increase of the radius of the hydrated ion and not to its crystallographic radius:[3]

$$D(Cs^+) > D(Rb^+) > D(K^+) > D(Na^+) > D(Li^+);$$
$$D(Na^+) > D(Ca^{2+}) > D(Y^{3+}) > D(Th^{4+})$$

However, for a low water content in moderately hydrophilic polymers, the sequence of the diffusion parameters can be inverted. For example, the decrease in the diffusion coefficients in polyamides (nylon-6) corresponds to the increase of the crystallographic radii of the singly charged cations Na^+, Rb^+, and Cs^+.[29] In exactly the same way, the activation energy for conduction by salts in nylon-6,6 and nylon-6 increased with increase in the crystallographic radius (Table 2). This result made it possible to conclude that there is no hydration, or the latter is extremely limited, in polyamides containing not more than 8% of water.[29]

Table 2. The activation energies for electrical conduction by various salts in nylons (electrolye concentration 0.1 M).

Polymer	Activation energy, kJ mol^{-1}			
	LiCl	NaCl	KCl	RbCl
Nylon 6	44.0	54.4	59.2	65.2
Nylon 6,6	49.4	54.5	—	57.0

With a high moisture content (ϕ_w = 0.7–0.9) in the same polymer, namely poly(vinyl alcohol), the mutual diffusion coefficients, determined interferometrically, increase in the sequence

$$D(K^+) > D(H_2O) > D(Na^+) > D(Mg^{2+}),$$

i.e. the same sequence as that corresponding to the increase of the radius of the hydrated ion (0.27, 0.30, 0.35, and 0.42 nm respectively), while in the presence of a low moisture content (ϕ_w = 0.1–0.2) the same diffusion parameters increase in conformity with the increase in the crystallographic radius[30] in the sequence

$$D(Mg^{2+}) > D(Na^+) > D(H_2O) > D(K^+).$$

Information about the state of the ion in a polymer matrix and about its diffusional mobility can be obtained directly by EPR spectroscopy. However, we may note that this method is applicable only to a limited number of paramagnetic ions such as Cu^{2+}, Mn^{2+}, Fe^{2+}, VO^{2+}, etc. Nevertheless, the extensive possibilities and high sensitivity of EPR spectroscopy made it one of the most promising methods for the investigation of the state of an electrolyte in a polymer, which has come to be widely used in physicochemical and biological research.[31,32]

The degree of interaction of water molecules with ions in a polymer matrix can be estimated quantitatively by analysing the dependence of the chemical shift of the proton signal, recorded by NMR, on temperature, moisture content, the nature of the ion, and certain other parameters. The position of the ^1H NMR signal of the water sorbed by the polymer depends on the capacity of the diffusing ion for hydration. The greater the polarising power of the cations, the greater the downfield shift of the signal. If electrostatic forces are mainly responsible for the polarisation of water molecules near the ion, the chemical shift should be proportional to the ratio of the ionic charge to the square of the crystallographic radius of the ion, i.e. the distance from the centre of the ion to the nearest molecule (z_i/r^2). Such a relation has been observed for a series of alkali and alkaline earth metal cations in the KU-2 cation-exchange resin.[33] The Rb^+ and Cs^+ ions, which have such large radii that electrostatic forces become weaker than those governing the interaction of the water molecules with one another and with the functional groups of the polymer, are an exception. An analogous linear relation has been observed also for anions.

In the course of the desorption of water from the polymer, the hydration shell of the ion is disrupted. The dielectric constant of the system falls and the dissociating cation–anion pair acts on water as a dipole and not as individual point charges. The position of the signal of the water protons undergoes a sharp upfield shift in this case. At a water concentration in the polymer approximately equal to two water molecules per ion and less, the NMR method does not make it possible to estimate the chemical shift as a consequence of the broadening of the resonance lines in the proton, which restricts the application of the method to moderately and weakly swelling polymers.[33]

(b) Dissociation of the electrolyte. The state of the electrolyte in a polymer is determined by the ratio of its ionised and unionised forms, i.e. by the degree of its ionisation. Other conditions being equal, the degree of ionisation depends on the electrolyte concentration. It is therefore useful to characterise the ionisation of an acid or base by the thermodynamic dissociation constant, which determines the strength of the given electrolyte in the diffusion medium and does not vary with concentration.

Depending on whether the electrolyte exists in the polymer in a dissociated form or as neutral molecules, the mechanism of the diffusional transport varies. For example, in the case of an acid, dissociation leads to the appearance in the system of the most mobile form of the protons. In addition, many degradative processes occurring in the polymer via an acid or base-catalysed mechanism are also determined by the concentration of hydroxide and hydronium ions.[15] Information about the state of the electrolyte in the polymer is therefore extremely important not only for the understanding of the diffusion mechanism but also for the prediction of changes in the system as a whole (decrease of the molecular weight and viscosity, a change in the ratio of the crystalline and amorphous phases, etc.).

The methods are known for the determination of the ionisation constant of an electrolyte in hydrophilic polymers: the ion-exchange method,[34] the spectrophotometric (indicator) method, and the conductimetric method.[35]

Table 3 presents the pK for certain electrolytes in hydrophilic polymers saturated with water. It is noteworthy that the dissociation constants of electrolytes hardly differ from the corresponding parameters in pure water in all the cases considered. This effect can apparently be accounted for by the shielding influence of water, which prevents the interaction of the electrolyte with the polymer molecule.[35]

5. Dependence of Diffusion Coefficients on the Electrolyte Concentration

The concentration dependence of diffusion coefficients characterises the features of electrolyte transport in hydrophilic polymers. In the general case its manifestation is due to the following factors: the differences between the mobilities of the dissociated and undissociated forms of the electrolyte; the non-ideal thermodynamic behaviour of the polymer–electrolyte solution system; the interaction of the ions with the functional groups of the polymer; the change in the structure of the polymer as a result of swelling.[36]

Table 3. The ionisation constants of electrolytes in hydrophilic polymers (pK) and in water (pK_w).

Electrolyte	Polymer matrix	c_w, wt.%	pK_w	pK	Method	Refs.
Glycine	KU-2 cation exchanger	60	2.34	2.49	1	[34]
Lysine	ditto	60	2.18	2.71	1	[34]
Lysine	»	60	8.95	9.06	1	[34]
Glutamic acid	»	60	2.18	2.12	1	[34]
α-Alanine	»	60	2.34	2.45	1	[34]
μ-Nitroaniline	Dowex 50 x 1	60	2.51	2.60	2	[3]
μ-Nitroaniline	PVA	78	2.51	2.59	2	[35]
H_3PO_4	»	78	2.12	2.14	3	[35]
H_3PO_4	»	38	2.12	2.15	3	[35]

Notation. Methods: 1) ion exchange; 2) spectrophotometric; 3) conductimetric; c_w = water content in the polymer.

(a) The influence of dissociation on the diffusional transport of the electrolyte. In a hydrophilic polymer the electrolyte can exist in partly or fully dissociated states. If the diffusing species formed as a result of the dissociation of the electrolyte have different mobilities, then the overall mobility of the electrolyte should be determined by the degree of its dissociation α_c:

$$D=\alpha_c D_s+(1-\alpha_c)D^u, \tag{6}$$

where

$$D_s=\frac{2D_C D_A\,(z_C-z_A)}{z_C D_C-z_A D_A}, \tag{7}$$

where D_A and D_C are the diffusion coefficients, z_A and z_C are the charges of the anion and cation respectively, and D^u is the diffusion coefficient of the undissociated species.

In order to account for the concentration dependence of the diffusion coefficients in the polymer, we shall formulate Fick's equation as follows:[37]

$$J_{H_mA}=-\sum_{m=1}^{m}[D_{H^+(A^{m-})}\nabla c_{H^+(A^{m-})}-D^u_{H_mA}\nabla c^u_{H_mA}], \tag{8}$$

where $D_{H^+(A^{m-})}$ and $D^u_{H_mA}$ are the diffusion coefficients of the dissociated and undissociated forms of the acid H_mA respectively, $c_{H^+(A^{m-})}$ and $c^u_{H_mA}$ are the concentrations of the corresponding forms, and J_{H_mA} is the flux of the diffusing acid. In all subsequent examples, the diffusion coefficients will be assumed to be constant.

In solutions with centimolar concentrations, hydrochloric acid is almost fully dissociated and Eqn.(8) becomes

$$J_{HCl}=-D_{H^+(Cl^-)}\nabla c_{H^+}. \tag{9}$$

Here

$$D_{H^+(Cl^-)}=2\cdot D_{H^+}D_{Cl^-}/(D_{H^+}+D_{Cl^-}) \quad \text{and} \quad c_{H^+}=c_{Cl^-}=c_{HCl}.$$

Eqn.(9) demonstrates the constancy of the diffusion coefficients of any strong acid in strongly swelling hydrophilic polymers. The absence of a concentration dependence of $D_{H^+(A^-)}$ has been observed experimentally for hydrochloric and trichloracetic acids.[3]

In the experimental concentration range, the strong dibasic acid H_2SO_4 undergoes appreciable dissociation of the second proton and the hydrogen ions diffusing in a neutral polymer matrix are surrounded by SO_4^{2-} and HSO_4^- ions. In this case Eqn.(8) makes it possible to obtain an expression for the effective diffusion coefficient:

$$D_{eff}=D_{HSO_4^-}\left[1+\frac{(\beta-1)}{(1+c_{H^+}/2K_2)^2}\right], \qquad (10)$$

where $K_2 = 1.25 \times 10^{-2}$ is the second dissociation constant of sulphuric acid and $\beta = D_{SO_4^{2-}}/D_{HSO_4^-}$ is the ratio of the diffusion coefficients of the individual ions.[37]

Analysis of Eqn.(10) shows that, if $\beta = 1$, i.e. when $D_{SO_4^{2-}} = D_{HSO_4^-}$, a single diffusion coefficient would be sufficient for the description of diffusional transport. At low acid concentrations $c_{H^+} \ll K_2/2$ and $D_{eff} = D_{HSO_4^-}\beta = D_{SO_4^{2-}}$. Indeed, the fraction of SO_4^{2-} ions in the bulk phase increases with increasing dilution of H_2SO_4 and in the limit transport involves only bivalent ions. On the other hand, at high acid concentrations, where $c_{H^+} \gg K_2/2$, the SO_4^{2-} ions are almost absent. Graphical solution of Eqn.(10) in terms of the variables D_{eff} and $(1 + c_{H^+}/2K_2)^{-2}$ made it possible to determine β, $D_{HSO_4^-}$, and $D_{SO_4^{2-}}$, which are 0.15, 5.9×10^{-10} $m^2\ s^{-1}$, and 0.9×10^{-10} $m^2\ s^{-1}$ respectively.[37] The lower diffusion coefficient of the bivalent SO_4^{2-} ion compared with that of the HSO_4^- ion indicates an increase of the diffusional resistance of the medium as a consequence of the increased hydration of multicharged ions and also stronger electrostatic and specific interactions in the polymer matrix.

In the case of phosphoric acid, which is weaker than the acids examined above, Eqn.(8) assumes the following form:

$$D_{eff}=D_{H^+(H_2PO_4^-)}\left[1+\frac{2\beta_1}{K_1}c_{H^+}\right], \qquad (11)$$

where $K_1 = 7.51 \times 10^{-3}$ is the first dissociation constant of phosphoric acid and $\beta_1 = D_{H^+(H_2PO_4^-)}/D_u$. Eqn.(11) predicts a linear increase of the diffusion coefficients with increasing concentration, which has indeed been observed in the transport of H_3PO_4 in water-saturated PVA films.

A linear increase of D_{eff} with increasing concentration c_{H^+} is observed for H_3PO_4 in the range of moderate concentrations, but in highly dilute solutions ($c_{H^+} = 2.5 \times 10^{-3}$ equiv. dm^3) there is an appreciable deviation from linearity. This effect has been explained[37] by the specific binding of the diffusing acid species in the polymer matrix.

For the almost fully dissociated acids HCl and CCl_3COOH as well as for the undissociated acetic acid CH_3COOH, there is no concentration dependence of the diffusion coefficients over the entire experimental concentration range.

In conclusion of this Section, we present in Table 4 the diffusion parameters of a series of acids of different types, determined in PVA films containing 75–78% of water. For comparison, the corresponding diffusion coefficients of the same acids in pure water are also quoted. Comparison of the diffusion parameters of different organic acids indicates the important role of the size of the diffusing species. The molecular diameter increases on passing from acetic to toluene-*p*-sulphonic acid, while the diffusion coefficients diminish in the same sequence.

Table 4. Diffusion parameters of acids in PVA films containing 75–78% of water ($\bar{D}$) and in pure water (D^0).[3]

Acid	$10^{10}\bar{D}$, m^2s^{-1}	$10^{10}D^0$, m^2s^{-1}	$\bar{D}/D^0$
$H^+(Cl^-)$	14.0	30.0	0.47
HSO_4^-	5.9	12.3	0.48
CH_3COOH	4.1	12.0	0.34
$H^+(ClCH_2COO^-)$	3.7	11.1	0.33
$H^+(Cl_3CCOO^-)$	3.2	10.4	0.31
SO_4^{2-}	0.90	2.2	0.41
H_3C–C$_6$H$_4$–SO_3H	0.75	—	—

III. DIFFUSION IN MODERATELY HYDROPHILIC POLYMERS

Moderately hydrophilic polymers contain a limited number of polar groups. Typical examples of polymers of this class are the polyamides, the amount of water which they absorb under normal conditions being 2–10%. Numerous studies of the sorption and diffusion of electrolytes have been carried out on polyamide specimens, which reflects the great interest of investigators in the problem of dyeing by acid and basic dyes.[38] Polyamide membranes are widely used in dialysis and reverse osmotic systems.[39] The purely technological problems involving the search for the optimum dyeing, purification, or separation conditions give rise to a problem of great theoretical importance, namely that of the study of the mechanism of the interaction of low-molecular-weight components in a polymer matrix.

The characteristic features of the diffusion of charged species into polar polymers which distinguish the latter from non-polar polymers are related to the strong interaction of such species with the functional groups characteristic of, for example, the polyamides ($-NH_2$, $-COOH$, $-CONH-$). Such interaction may entail the complete loss of mobility by some of the diffusing ions or an exchange interaction with the functional group R in accordance with the scheme

$$R + E \underset{}{\overset{K}{\rightleftharpoons}} RE.$$

When the number of binding groups exceeds the number of electrolyte molecules (E), for example those of HCl in polyamide 6, the diffusion is retarded in accordance with the equations

$$\frac{\partial c}{\partial t}=D_{eff}\frac{\partial^2 c}{\partial x^2}; \quad D_{eff}=D/(1+K[R]_0), \qquad (12)$$

where D is the true diffusion coefficient, $[R_0]$ the concentration of the reacting groups in the polymer, K the exchange equilibrium constant, and x the diffusion coordinate.

For a correct interpretation of the results of diffusion experiments, it is essential to know the composition and state of the electrolyte and the nature and distribution of the polar groups of the polymer.

1. The Influence of the Ionogenic Groups of the Polymer on the Concentration Dependence of the Diffusion Coefficients

In the initial state the polyamide macromolecules contain unequal numbers of terminal amino-groups B_0 and carboxy-groups A_0. Some of the amino- and carboxy-groups are linked to one another in a zwitter-ionic form. The sorption of acid under conditions where $B_0 > A_0$ therefore includes three consecutive stages:

$$\begin{gathered} R{-}NH_2 + HCl \xrightarrow{(a)} R{-}NH_3Cl, \\ R{-}NH_3^+{-}R{-}COO^- + HCl \xrightarrow{(b)} R{-}COOH + R{-}NH_3Cl, \\ R{-}CONH{-}R + HCl \xrightarrow{(c)} R{-}NH_3^+COO{-}R(Cl^-), \end{gathered} \qquad (13)$$

If $A_0 > B_0$ in the polymer, then only reactions (b) and (c) take place.

Despite a number of limitations, the proposed scheme (13) can explain certain experimental facts (see Zaikov et al.,[3] p.123). The role of a neutral electrolyte, for example KCl, present in the polymer has been examined by Crespo.[40]

As a result of the interaction of the diffusing ions with the ionogenic and polar groups of the polymer, a dependence of the mobility of the ions on the degree of binding of these groups (the degree of filling of the adsorption sites θ_f) is observed in the initial stages of the sorption process. With increased concentration of the acid in the polymer, the functional groups are deactivated in accordance with scheme (13) and their electrostatic and chemical influences on the diffusing ions and molecules diminish. When the acid concentration has passed through a critical region where the condition $c_{A_0} = c_{HA}$ holds, the diffusion coefficient of the electrolyte increases sharply. For example, the self-diffusion coefficient of sulphuric acid in the amine region of polyamide 6, measured by the radioactive isotope method, is described by the analytical expression[41]

$$D^*_{H_2SO_4} = \frac{K}{2K_2}\frac{\theta_f}{(1-\theta_f)}D^*_{HSO_4^-} + \left[1 - \frac{K}{2K_2}\left(\frac{\theta_f}{1-\theta_f}\right)\right]D^*_{SO_4^{2-}}, \qquad (14)$$

where θ_f is the degree of occupation of the terminal amino-groups and K/K_2 is the ratio of the equilibrium constant of reaction (a) in scheme (13) to the second dissociation constant of H_2SO_4. The agreement between the experimental and theoretical results can be seen from Fig.4. An analogous sharp increase in the effective diffusion coefficients in polyamides is observed predominantly for cations (protons) in the HBr–polyamide-6,6 and sulphuric acid–keratin systems.[3]

In diffusion systems where there is an equilibrium between the freely diffusing ions and ions bound to the functional groups of the polymer, the activity coefficient is determined by the ratio $\gamma = D_{eff}/D_i$, where D_i is the diffusion coefficient of the free ion, which is independent of the concentration.

As regards inorganic acid anions, the concentration dependence of their diffusion coefficients is less marked. For example, the self-diffusion coefficient of the Br^- ions in the amine region of polyamide 6,6 is almost independent of the acid concentration and increases slightly in the amine region (from 6×10^{-15} to 10^{-14} m^2 s^{-1}). The diffusion coefficient of the Cl^- ion in polyamide 6 at 70 °C also depends only slightly on the concentration over a wide range of degrees of saturation of the adsorption sites:[3]

θ_f	0.19	0.40	0.75	0.82
$10^{11}D_{Cl^-}$, m^{2}s^{-1}	0.40	0.45	0.49	0.52

The coefficients $D_{SO_4^{2-}}$ and $D_{HSO_4^-}$ depend more markedly on the concentration but even their concentration dependence is less pronounced than that of D_{H^+}.

The complex dependence of the diffusion coefficients of the anions of organic dyes on concentration reflects the interaction of the moving anions not only with the polymer matrix but also with one another.

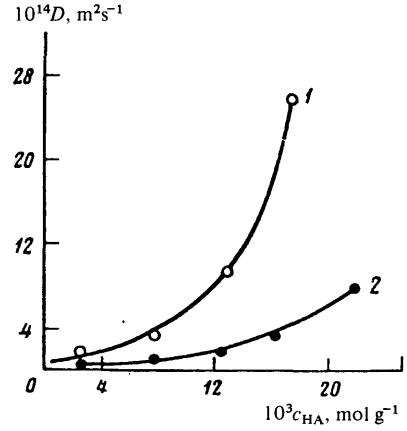

Figure 4. Dependence of the diffusion coefficients of sulphuric acid in polyamide 6,6 at 25 °C on its concentration;[41] 1) $D(H_2SO_4)$; 2) $D(SO_4^{2-})$; circles—experiment; continuous curves—calculated data.

The diffusion of organic acids has been studied in less detail than that of inorganic acids, but the relations obtained suggest that the mechanism of their sorption in the amine region is the same as that of inorganic acids. Table 5 presents the diffusion and thermodynamic parameters for the sorption of weak organic acids by polyamide 6,6.

The mobility of ions in water is determined by the size of the hydration shell which is greater for ions with a smaller crystallographic radius. However, the mobility of cations in moderately hydrophilic polymers diminishes with decrease of the crystallographic radius.[42] This fact shows that the cations present in the polymer lack a hydration shell.

2. The Equilibrium Sorption of Electrolytes

The "equipotential internal solution" model has been one of the first to be proposed for simple inorganic ions sorbed by moderately hydrophilic polymers. According to this model, an electrolyte solution, analogous to the external solution but having a potential $\Delta\phi$ relative to the latter, exists in the polymer:

$$K_p = \bar{c}_{Na}/c_{Na} = c_{Cl}/\bar{c}_{Cl} = \exp[\sinh^{-1}(c_f/2c_{NaCl})], \qquad (15)$$

This equation agrees quite well with experiment at moderate and high electrolyte concentrations in the polymer. At high dilutions, appreciable discrepancies are observed between the experimental and calculated K_p.[43]

In the Gilbert–Ridal theory (see Zaikov et al.,[3] p.189), it is assumed that ions are adsorbed on a limited number of statistically distributed ionogenic groups of the polymer in accordance with the equation

$$\lg\left(\frac{\theta_f}{1-\theta_f}\right) = \lg c_{CA} + \frac{W_p + W_v - e\Delta\varphi}{2.3kT}, \qquad (16)$$

where W_p and W_v are the polarisation and van der Waals interaction energies respectively, e is the electronic charge, and c_{CA} the concentration of the electrolyte.

The ion-exchange model has been proposed by Myagkov and Pakshver (see Zaikov et al., [3] Chapter 5) to account for the sorption of HCl, KCH, naphthalene-2-sulphonic acid, and certain dyes by polyamide 6. This model predicts that

$$\lg[x(x_0-x)^{-1}] = \lg k - 2\,\mathrm{pH},$$

where x_0 and x are the total number of functional groups and the number of such groups bound to the ion respectively and k is the sorption constant.

The models mentioned above make it possible to obtain only a limited agreement between the calculated and experimental data, which is the reason for the development of the Mathieson–Whewell polyelectrolyte model (quoted after Zaikov et al.[3]). The authors of this model postulate that the energy required to remove H^+ from the polymer to the solution depends on the electrostatic and osmotic interactions of the electrolyte in the polymer and on the chemical affinity (the difference between the standard chemical potentials of H^+ in the polymer and in the solution $\Delta\mu_H^0$). For a partly dissociating group in the polymer, the following equation is frequently used:

$$\mathrm{pH} = \mathrm{p}K_A - \lg[(1-\alpha_c)\alpha_c^{-1}] - \frac{0.434}{RT}(zF\Delta\varphi + \Delta\mu_H^0), \qquad (17)$$

where z is the charge on the group, K_A the dissociation constant, T the absolute temperature, F the Faraday, and R the gas constant.

Association of groups bearing unlike charges in the polymer distorts the potential and its distribution in the membrane. There exist two ways of taking into account association. According to the first procedure, a correction coefficient β, characteristing the fraction of charged groups incorporated in the ion pairs (associated species), is introduced in order to describe the potential. In this case the electrostatic factor is determined by the coefficient $-0.0434F\phi_m\beta/RT$, where ϕ_m is the average membrane potential. However, since β is difficult to calculate because it depends on the electrolyte concentration and hence on the coordinate of the diffusion process, it is more convenient to employ two kinds of carboxy-groups (in the general case acid groups)—free and paired, which dissociate with their own dissociation constants K_p and K_q respectively [see Eqn.(17)]. In this case the concept of a homogeneous membrane potential ϕ_m is retained.

The molecular weights of polymers dissociating only at the terminal groups influence the solubility of the electrolyte. If it is assumed that the accessibility of these groups, the pK, and $\Delta\mu_H^0$ are independent of the degree of polymerisation, then Eqns.(15) and (17) make it possible to relate the degree of polymerisation and the content of end groups c_f to the acid concentration:

$$\mathrm{pH} = \mathrm{const} - 0.434\,\sinh^{-1}(c_f/2c_s), \qquad (18)$$

When $c_f/2c_S > 200$, i.e. when the concentration of the added salt c_S is low, $\sinh^{-1}(c_f/2c_S)$ can be replaced by the corresponding logarithmic relation:

$$\mathrm{pH} = \mathrm{const} - \ln(c_f/c_s). \qquad (19)$$

Graphical solution of Eqn.(19) with a constant c_S, which is presented in Fig.5, indicates a satisfactory agreement between theory and experiment.

In the absence of specific interaction, titration curves make it possible to estimate the pK of the acid groups of the polymer. For example, for keratin twice the pH at the midpoint of the titration curve (i.e. on the plot of pH against $\bar{c}_{HA}$) is equal to the pK of glutamic acid, which can serve as a model of the elementary unit of this polymer. However, for adipic acid, the model of the elementary unit of polyamide 6,6, such an equaltity has not been observed even if a correction is made for the shift of the isoelectric point of this polymer as a consequence of the inequality of the numbers of its acid and basic groups. The most probable cause of this discrepancy is a lower dielectric constant ε in polyamide 6,6 compared with the keratin matrix, where ε does not differ markedly from its value in water.

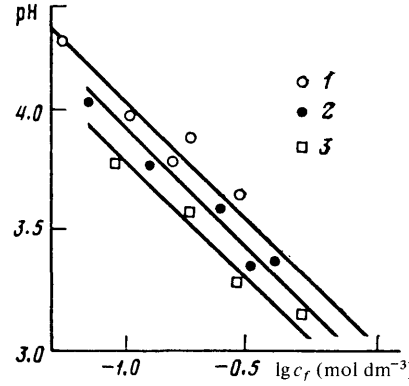

Figure 5. The influence of the degree of polymerisation (of the content of end groups) on the pH in the PA–HCl system for different degrees of ionisation: 1) 0.7; 2) 0.6; 3) 0.5.[3]

Table 5. Diffusion coefficients (D), activation energies for diffusion (E_D), changes in the chemical potential ($\Delta\mu$), and heats of sorption (ΔH) of organic acids in polyamides 6,6 at 60 °C (see Zaikov et al., [3] Chapter 5).

Acid	$10^{13}D$, m^{2}s^{-1}	E_D, kcal mol^{-1}	$\Delta\mu$, kcal mol^{-1}	ΔH, kcal mol^{-1}
Formic	13.2	2.8	0.18	0.4
Acetic	18.1	7.7	−0.41	−0.4
Propionic	14.4	7.2	−0.42	−0.24
Butyric	10.0	6.9	−0.41	−0.70
Salicylic	2.7	21	−1.8	−1.9
Benzoic*	0.3	12.9	—	−3.2
Sorbic**	2.6	3.1	−1.9	−9.8

*Polyamide 610, temperature 45 °C.
**Temperature 55 °C.

Table 5 lists the chemical affinities $\Delta\mu$ of various acids for the polymer, calculated by Eqn.(17). Apart from their theoretical interest, these results are of practical value for the estimation of the stabilities of dyed articles.

IV. DIFFUSION IN HYDROPHOBIC POLYMERS

Polymers of this class are characterised by a high chemical stability in relation to electrolyte solutions. The low polarity of their macromolecules is responsible for the low solubility

of water and electrolytes in hydrophobic polymers, for example, in polyolefins, polyesters, and fluorinated plastics (PTFE). As a consequence of the low polarity of the polymer medium, the acids, bases, and salts contained in it are associated. In this connection, one may note that polymers resistant to acid hydrolysis are as a rule hydrophobic; however, the opposite claim is invalid, because not every hydrophobic polymer is resistant to acid hydrolysis. An example of this is provided by polysiloxanes (see Zaikov et al.,[3] p.147).

1. The Influence of the Nature of the Electrolyte

The most characteristic feature of the diffusional transport of electrolytes in hydrophobic polymers is its selectivity. For example, the permeation of nitric acid through a film of ftoroplast-42 (a type of PTFE) is recorded after ~10^3 s, while the permeation of sulphuric acid through a similar film can be observed only after a year.[44]

Almost all hydrophobic polymers are readily permeable to hydrochloric, hydrofluoric, nitric, acetic, and fluorosilicic acids and to ammonium hydroxide solutions. Sulphuric and phosphoric acids, inorganic bases, and salts diffuse much more slowly (see Reitlinger,[4] p.45). For a series of electrolytes, for example in the polypropylene–KCl system,[47] the permeability could not be measured at all apparently owing to the low solubility of the electrolyte and the inadequate sensitivity of the method of measurement.

The permeability of hydrophobic polymers and the vapour pressures of the electrolytes were first compared by Shterenzon and co-workers.[47,48] Electrolytes characterised by a high vapour pressure diffuse into polymers with coefficients close to the diffusion coefficients of water (D_{H_2O}). Another group of electrolytes, having low volatilities, is transported in polymers with diffusion coefficients much lower than those of water in the same polymer. An analogous classification of electrolytes into "strongly diffusing" and "weakly diffusing" has been proposed by Alt.[49] It is important to note the arbitrary nature of the subdivision of electrolytes into volatile and involatile. At high temperatures and concentrations a typical involatile electrolyte such as sulphuric acid behaves as a volatile electrolyte as regards transport.

The influence of the nature of the volatile electrolyte on its diffusion coefficient is non-specific and is expressed solely by the dependence of the diffusion coefficient on the size of the diffusing species (see Zaikov et al.,[3] p.155).

The concentration dependence of the diffusion coefficient of HCl in low-density polyethylene (LDPE) has been investigated with the latter in contact both with a dry gas at different partial pressures and with an aqueous solution.[50] It was noted that the integral diffusion coefficients of hydrogen chloride diffusing from aqueous solutions increase with increasing concentration of hydrochloric acid, tending to the constant value found for the dry gas. In order to account for this result, a comparative study was made of the equilibrium sorption of HCl from a dry gaseous phase and from aqueous solution. At identical vapour pressures, a greater amount of HCl is sorbed from the solution than from the gas phase. This difference has been explained by the fact that, in the presence of water, some of the electrolyte molecules permeating into the polymer are bound in the form of associated species and an additional amount of HCl passes from the solution to the polymer in order to establish an equilibrium. The overall amount of the sorbed acid (c_{HCl}) is in this case determined by the equation

$$c_{HCl} = c_F + MK_H c_F (p_w k_w)^n \qquad (20)$$

where c_F is the concentration of free HCl not bound in the hydrates, M the molecular weight of HCl, K_H the equilibrium constant of the hydrate formation process, k_w the constant for the sorption of water by the polymer, p_w the partial pressure of water vapour over the solution, and n the number of water molecules in the hydrate, which is 5.0 ± 1.3 for the given system.[50]

It is seen from Eqn.(20) that the ratio of the hydrated and unhydrated forms of the acid diminishes with decrease of the partial pressure of water vapour.

The proposed model makes it possible to obtain an expression for the effective diffusion coefficient of HCl in polyethylene and to describe quantitatively its concentration dependence:

$$\bar{D}_{HCl} = \frac{D^0_{HCl}}{1 + MK_H (k_w p_w)^n}, \qquad (21)$$

where D^0_{HCl} is the diffusion coefficient of dry gaseous HCl. The average number of water molecules in the HCl hydrate, calculated from the results of kinetic (diffusion) measurements, is 4.3 ± 1.7, which is fairly close to the values of n obtained from equilibrium sorption data.[50]

The possibility of the existence of hydrates of volatile electrolytes in hydrophobic polymers was pointed out by Dolezel,[51] who observed a sharp increase of D_{HNO_3} in poly(vinyl chloride) in the presence of a 50% concentration of the acid.

Murov et al.[52] proposed a model involving the parallel-consecutive binding of the electrolyte and water in hydrophobic polymers of the type of polyethylene and polypropylene (PP). According to this model, the non-stationary flux of water molecules from dilute solutions of the volatile electrolyte, subject to the condition $p_w \gg p_s$, can exceed the non-stationary flux of the electrolyte (consecutive binding scheme). In this case it is assumed that the electrolyte diffuses in the hydrated polymer matrix and the probability of the existence of free electrolyte molecules is lower the higher the concentration of water in the polymer. With increase of the concentration in the solution in the external phase, the water and the electrolyte vapour pressures become similar ($p_w \cong p_s$) and the components are bound in the polymer in accordance with the parallel kinetic scheme. The transport of unhydrated electrolyte species is in such cases facilitated.

A further development of ideas concerning the interaction of water and the electrolyte in the polymer was achieved by Shterenzon (see Zaikov et al.,[3] p.159). If it is assumed that the composition of the hydrated complex $HA \cdot xH_2O$ is analogous to that of the external solution, then

$$\lambda_D^2 = r_0 \left[\frac{p_s}{p_s^0} \left(\frac{p_w}{p_w^0} \right)^x \right]^a \qquad (22)$$

where λ_D is the non-stationary permeability coefficient,[3] reflecting the rate of movement of the diffusion front of the electrolyte in the polymer, p_w^0 and p_s^0 are the vapour pressures of the pure electrolyte and pure water respectively, r_0 and a are empirical constants, and x is the number of moles of water per mole of the acid.

The calculated and experimental values of λ_D agreed satisfactorily over a wide range of HCl, HF, HNO_3, and H_2SiF_6 concentrations. Here it is appropriate to emphasise that the concentration dependence of λ_D(HCl) has the same form in dilute (7%) and concentrated (29%) solutions, which makes it possible to put forward the hypothesis of a transition of the diffusion mechanism from consecutive to parallel binding.

2. The Influence of the Nature of the Polymer

The chemical structure of hydrophobic polymers influences only weakly the rate of diffusional transport. In most cases the difference between the diffusion parameters is determined by the difference between the morphologies of the polymers. For example, the extremum in the dependence of the sorption of nitric acid by vinylidene fluoride–chlorotrifluoroethylene and vinylidene chloride–hexafluoropropene copolymers on composition can be accounted for by the transformation of the structure into an amorphous form[53] (the permeability constants of the membranes have been published,[15] p.141).

The polar groups present in a polymer as a result of oxidation alter significantly the diffusion characteristics of hydrophobic polymers. It has been shown,[54] that, with increase of the concentration of the carbonyl groups in polyethylene on oxidation, its electrical conductivity and sorption capacity with respect to salt solutions also increase. Polyethylene films oxidised by sulphur trioxide absorb up to 20% of water and behave like polycarboxylic acid, manifesting, in particular, ion-exchange properties.

The introduction of a filler into the polymer matrix can decrease the mobility of the macromolecules and can lead to the appearance of defects in the polymeric diffusion medium and to the direct interaction of the diffusing species with the additives. Polyethylene containing 16% of graphite, which is inert with respect to the polymer and the electrolyte, is 10% less permeable than unfilled polyethylene. The introduction of a filler without a high adhesion capacity towards the polymer, namely chromium oxide, does not decrease but actually increases the rate of diffusion of HCl and especially HF. Dyeing of a chlororubber coating with TiO_2 also entails an increase of its permeability to Cl^- ions.[55] Zaikov et al.[3] (Chapter 6) have reviewed investigations of the interaction of electrolyte components with the additives introduced into a hydrophobic polymer (hydrophilic fillers of the type of talc and CaO, various surfactants, and plasticisers).

Table 6. The activation energies for the diffusion of electrolytes (Zaikov et al.,[3] Chapter 6).

Polymer	Electrolyte	c, wt.%	E_D, kJ mol^{-1}
Poly(ethylene terephthalate)	H_2SO_4	53	50
PTFE	HNO_3	98	18.8 (>323 K) 50.6 (<323 K)
PE	HNO_3	98	41.8
PE	H_2SO_4	10	55
PP	H_2SO_4	10	31

3. The Influence of Temperature

For many of the systems investigated, a linear relation has been observed between $\lg D_S$ and $1/T$, which makes it possible to calculate the activation energy for diffusion E_D (Table 6). A characteristic feature of the diffusion of electrolytes in polymers is manifested by the fact that the diffusion parameters are determined simultaneously by the electrolyte concentration in the polymer and the experimental temperature. It has been reported[56] that, for a non-steady state process involving the permeation of HCl into high-density polyethylene, E_D varies from 49.3 to 39 kJ mol^{-1} with increase in the concentration of the acid from 15 to 30 wt.%. An empirical equation for the dependence of the non-stationary permeation coefficient λ_D on temperature and concentration (pressure) of the electrolyte has the following form:

$$\lambda_D = A_0 e^{(U/RT)}, \quad (23)$$

where A_0 is an empirical parameter which depends on the concentration or vapour pressure of the electrolyte and U is the energy parameter. Here it is important to note that the pre-exponential factor depends on concentration and temperature (see Zaikov et al.,[3] p.161), which has been confirmed by a series of experiments.[57]

4. The Interaction of Diffusion Fluxes. Countercurrent Diffusion

The interaction of the diffusion fluxes of water and the electrolyte is manifested by the desorption of the latter into water from hydrophobic specimens. Thus a polyethylene specimen subjected to preliminary saturation with hydrochloric acid desorbs HCl into an aqueous environment extremely slowly, while the desorption in a stream of dry air is significantly faster. A detailed study[58] has been made of the phenomenon of the temporary cessation of the release of acid from the film under the conditions of the countercurrent diffusion of water. The interaction of water and the acid in the polymer increases the delay time θ and hence leads to unjustifiably low diffusion coefficients $D = l^2/6\theta$, where l is the thickness of the polymer film. Extrapolation of $\lg \theta$ to zero water vapour pressure p_W is therefore of considerable interest, since it makes it possible to estimate θ for the electrolyte without taking into account the binding to water.[12]

When hydrophobic polymers are used as protective coatings, the specimens become turbid in the presence of many electrolytes. The appearance of turbidity is initially very rapid and then slows down, taking place over a period of several tens and hundreds of hours. The intensity of the turbidity depends on the nature of the polymer and the electrolyte and also on the concentration of the latter. Sulphuric, phosphoric, and acetic acids and ammonia do not cause turbidity, while the countercurrent diffusion of hydrochloric, nitric, and hydrofluoric acids in the region of an ~30% concentration leads to the formation of the electrolyte solution phase in the case of LPPE.[47]

Just as a mist is formed in the gas phase, in hydrophobic polymers there is a possibility of the appearance of tiny droplets resulting from the association of the volatile electrolyte with water. However, the formation of a new phase within the polymer requires the expenditure of energy on the deformation of its structure. In polymers with different physicomechanical characteristics, identical expenditures of the energy liberated as a result of the interaction of water and electrolyte lead to the formation of drops of different size. In certain cases the resistance of the polymer to deformation is so great that the new phase cannot be formed.[47] The enthalpy ΔH^0 of the process $(CA)_{gas} \rightleftarrows (CA)_{soln}$ has been suggested as a quantitative criterion of the possibility of forming clusters in hydrophobic polymers.[47] The ΔH^0 for the electrolytes investigated can be arranged in the sequence

$$\Delta H^0_{NH_3} > \Delta H^0_{HNO_3} > \Delta H^0_{HCl} > \Delta H^0_{NH_4Cl}.$$

In the countercurrent diffusion of water and ammonia, the liberated energy (10 kJ mol^{-1}) is insufficient for the formation of drops, while the energy evolved as a result of the interaction of the HCl and ammonia fluxes is so great that a

continuous layer of ammonium chloride is formed within the polyethylene film, disrupting the polymer matrix. In practice the above effects are used to obtain X-ray contrast materials and for the layer-by-layer cleavage of polymer membranes in microscopic studies.

5. The Sorption of the Electrolyte

For an approximate estimate of the concentration of the sorbed electrolyte in the amorphous phase of the polymer, it has been suggested[47] that a simplified version of the Flory equation be employed:

$$-\ln \varphi_s = 1 + \frac{\bar{v}_s (\delta_s - \delta_p)^2}{RT}, \qquad (24)$$

where δ is the solubility parameter, ϕ and $\bar{v}$ are respectively the volume fraction and the molar volume of the ith component, and s and p are subscripts referring to the electrolyte and the polymer respectively. Eqn.(24) shows that the degree of equilibrium sorption of the electrolyte is greater the lower the modulus of the difference between the solubility parameters of the polymer and the electrolyte. For polyolefins $\delta_p = 16$, for pentaplast $\delta_p = 10$, and for sulphuric acid $\delta_s = 35$ $J^{1/2}cm^{-3/2}$. It follows from Eqn.(24) that the concentration of H_2SO_4 in pentaplast should exceed the concentration of acid in polyolefins by a factor of 40. The different permeabilities of pentaplast and polyethylene to H_2SO_4 indirectly support this.[3]

---o0o---

A quantitative description of the diffusion and solubility of electrolytes in polymers is an essential condition for the prediction of the chemical stability of the material and of the operating parameters of anticorrosion coatings (hydrophobic polymers). For the successful employment of medical polymers as implants and elements of artificial organs, information is also required about the equilibrium and kinetic parameters for the sorption of the components of the biological medium (on hydrophilic and moderately hydrophilic polymers). The optimisation of the dyeing and printing processes is impossible without a description of the diffusion in fabric materials.[59] The theory of membrane purification, separation, and concentration methods is also based on the diffusion mechanism in hydrophilic and moderately hydrophilic membranes.[60] One can claim with confidence that in the future our ideas about the diffusion of electrolytes in polymers will expand significantly in connection with the vigorous development of chemotronic systems and photochemical and mechanochemical energy converters.

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Modification of DNA by Alkylating Compounds

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The results of studies of the physicochemical properties of alkylating compounds—alkylnitrosoureas (ANU)—with a broad spectrum of biological activities (mutagenic, carcinogenic, and antitumour) as a result of the alkylation and carbamoylation of DNA as well as other cell components are presented. The identified chemical products of the interaction of ANU with DNA and its components are listed. The structural transformations of the DNA macromolecules as a consequence of their chemical modification are examined and the possible biological consequences of the modification of DNA by ANU are discussed. The bibliography includes 148 references.

CONTENTS

I. Introduction 898
II. Chemical and physicochemical properties of alkylnitrosoureas 898
III. Chemical products of the reactions of alkylnitrosoureas with DNA and its components 899
IV. Structural changes in DNA modified alkylnitrosoureas 900
V. Biological consequences of the chemical modification of DNA 902

I. INTRODUCTION

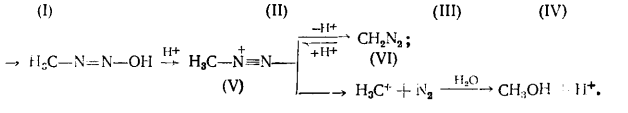
Alkylating compounds with a broad spectrum of biological activities have long attracted the attention of investigators. The knowledge of the mechanisms of the action of these compounds on the most important cell biopolymers will make possible their specific employment to achieve the desired effect. Among alkylating compounds, alkylnitrosoureas (ANU), which have been investigaged vigorously in recent years as chemical mutagens,[1-10] carcinogens,[11-17] and antitumour agents,[18-21] are of great interest.

Academician N.M.Emanuel' and his students have widely used for many years physicochemical and chemical kinetic methods in the study of many most important biological systems,[22-26] biochemical reactions,[27-29] and various pathological processes.[30-33] Their discovery of the antitumour properties of ANU and the introduction into clinical practice of *N*-methyl-*N*-nitrosourea (MNU) as a drug for the treatment of the undifferentiated cancer of the lung and lymphogranulomatosis[18] stimulated in recent years the wide-scale synthesis of new ANU derivatives and the study of the physicochemical properties and the molecular mechanism of the action of these compounds in order to discover ANU most effective in practical use.

One of the main (and perhaps most important) causes of the biological action of ANU may be reactions involving the interference with the functioning of the cell genome as a result of the modification of DNA due to the alkylation and carbamoylation of its macromolecule.

II. CHEMICAL AND PHYSICOCHEMICAL PROPERTIES OF ALKYLNITROSOUREAS

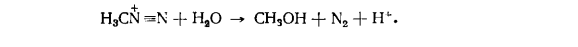
Certain reactions of ANU can be analysed in relation to one of the representatives of compounds of this class which have been investigated, namely MNU. It has been established that the ANU are readily hydrolysed in aqueous solutions and that the rate of hydrolysis changes significantly as a function of the composition of the medium, pH, temperature, and other factors. A general scheme for the actions of MNU in aqueous solution can be represented in the following manner:[34-41]



Under the influence of hydroxide ions, the proton is abstracted from the nitrogen atom of the MNU molecule (I) with formation of a urea anion (II), which is converted into the diazotate anion (III) and isocyanic acid (IV).

The first stage of the decomposition of MNU is in this instance rate-limiting and is of pseudofirst order. This serves as the basis for the method involving the titration of MNU with alkali,[37] which is used together with other chemical methods for the investigation of the kinetics of this reaction.[38,39] The anion (III) formed is converted into the methanediazonium cation (V) under the influence of protons. In a highly alkaline medium, diazomethane (VI), which is an alkylating agent, is formed.[40]

In a neutral medium, diazoalkanes are usually not formed and the methylating properties are in this instance due to the methanediazonium cation,[41] whose addition to nucleophiles is accompanied by the evolution of nitrogen. In an aqueous medium hydrolysis takes place with formation of methanol:



The rate of reaction of MNU in aqueous solution depends particularly on the pH of the solution and it has been established that in a Britton–Robinson buffer the half-life of MNU diminishes with increasing pH. The composition of the medium influences the reactions of MNU in aqueous solutions. In the presence of buffer mixtures (phosphate and phosphate-citrate buffers) an increase in the rate of reaction of MNU owing to the action of nucleophiles is observed.[42]

In an acid medium one of the products of the reaction of MNU is nitrous acid,[38,39] which is known to be capable of functioning

as a deaminating agent:[43]

$$\underset{\mathrm{CH_3}}{\mathrm{H_2NCONNO}} + \mathrm{H_2O} \xrightarrow{\mathrm{H^+}} \mathrm{HNO_2} + \underset{\mathrm{CH_3}}{\mathrm{H_2NCONH}}.$$

Thus, depending on the conditions, the reactions of MNU in various media can give rise to products of several types: diazomethane (pH > 7), and methanediazonium cation and isocyanic acid (pH ~ 7), and nitrous acid (pH < 7). In the reactions with nucleic acids and their components, these products can exhibit their characteristic properties and can modify the biomacromolecules.

Analysis of the chemical nature and electronic structure of MNU established that this compound possesses donor–acceptor properties, which may be responsible for the varied manifestations of the biological activity of MNU.

It has been demonstrated by quantum-chemical and EPR methods that the NO group in the MNU molecule can behave as an electron acceptor or donor.[44–46] When an electron is captured by the NO group, the following reactions can take place:

$$\mathrm{H_2NCON(CH_3)NO} + \bar{e} \rightarrow \mathrm{H_2NCON(CH_3)N\dot{O}} \rightarrow$$
$$\rightarrow \mathrm{H_2NCONH\dot{C}H_2} + \bar{N}O \rightarrow \mathrm{CH_2NH} + \dot{C}ONH_2 + \bar{N}O.$$

The radical $\dot{C}ONH_2$ can behave as a carbamoylating agent.

The electron-donating properties of MNU are due to the abstraction of an electron from the nitrogen atom of the NO group with formation of a radical-cation whose decomposition can apparently give rise to the following products:

$$\mathrm{H_2NCON(CH_3)NO} \xrightarrow{-\bar{e}} \mathrm{CH_3{-}N{=}N{-}O^{\cdot}} + [\mathrm{CONH_2}]^+ \rightarrow$$
$$\rightarrow \mathrm{CH_3{-}N{=}N{-}O^{\cdot}} + \mathrm{H^+} + \mathrm{HNCO} \rightarrow \mathrm{CH_3^+} + \mathrm{N_2} + {}^{\cdot}\mathrm{OH} + \mathrm{HNCO}.$$

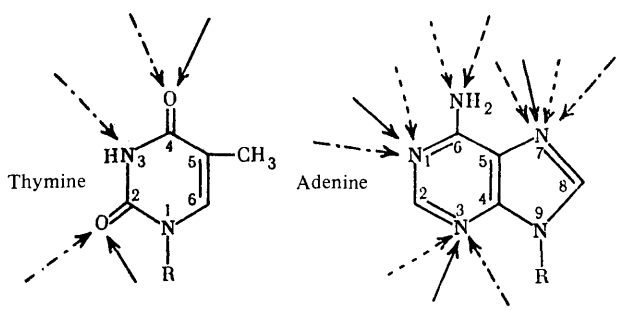
In this case the chemical reactivity of MNU is determined mainly by the radical $CH_3N = NO^{\cdot}$, whose interaction with biomacromolecules can lead to methylation. Carbamoylation takes place due to HNCO.

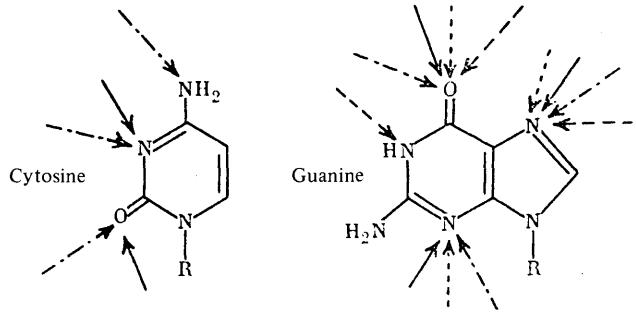
The radicals $\dot{C}ONH_2$, $CH_3{-}N = N\dot{O}$ and $H_2NCON(H)\dot{C}H_2$ have been detected by EPR in a frozen NMU solution under the conditions of the photosensitised electron transfer in the presence of an electron acceptor (donor).[45]

III. CHEMICAL PRODUCTS OF THE REACTIONS OF ALKYLNITROSOUREAS WITH DNA AND ITS COMPONENTS

In order to elucidate the molecular mechanism of the biological action of ANU, it is important to determine the principal sections of the biomacromolecules which may be modified by treatment with ANU. The first studies of the mechanism of the action of ANU derivatives were undertaken to investigate their alkylating properties.

The objects of study were nucleosides,[40,47] nucleotides,[48,49] polynucleotides,[50] and nucleic acids.[7] The observed sites where nucleic acid bases are alkylated can be represented schematically in the following manner (R represents the ribose or doxyribose residue):





The positions in which the bases are alkylated are indicated by arrows:
In nucleosides – – →
In nucleotides (polynucleotides) - - - →
In single-stranded DNA ——→
In double-stranded DNA –·–·→

The alkylation of triphosphate groups with formation of the monoethyl ATP ester (11% of the total amount of alkyl groups) has been demonstrated in model experiments with ATP and ethylnitrosourea (ENU).[49]

The possibility of alkylating DNA was first established in relation to the formation of 7-methylguanine in the reaction of DNA with MNU.[51] Later nine methylated derivatives were identified in an *in vitro* reaction of DNA with MNU: 1-methyladenosine, 3-methyladenine, 7-methyladenine, 3-methylguanine, 6-*O*-methyldeoxyguanosine, 7-methylguanine, 3-methyldeoxycytidine, 3-methylthymidine, and 4-*O*-methylthymidine. 3-Methyladenine (11.2% ^{14}C) and 7-methylguanine (75.7% ^{14}C) are formed in highest yields, while 4-*O*-methylthymidine (0.1% ^{14}C) is formed in the lowest yield. The amount of alkylated phosphate groups was 18% of the total radioactivity corresponding to DNA.[52,53]

It is noteworthy that, in those cases where MNU reacts with polynucleotides without a guanine residue, the contribution of the pathway involving the alkylation of phosphate groups increases sharply. For example, according to Shooter and Venitt,[54] the corresponding yield for the MNU-modified DNA is 18%, while according to other data, on treatment of polyadenylic acid with [$^{14}CH_3$]MNU, 23% of the yield is due to the alkylation of the bases and the remaining 77% is associated with the formation of phosphotriesters. The difference between the yields of the alkylated phosphate groups is frequently explained by the different experimental conditions and also by the instability of the products in alkaline media.[56]

The methyl and ethyl phosphotriesters are formed in DNA on treatment with the majority of alkylating carcinogens and are retained in it for a long time.[54,57] A dinucleotide containing alkylated phosphate groups has been isolated in the hydrolysis of DNA modified with MNU.[57]

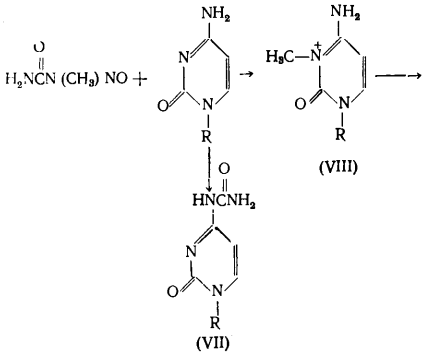
Comparative study of the reactivities of different alkylating compounds, namely dimethyl sulphate, diethyl sulphate, ENU, and MNU, in relation to the phosphodiester linkage in DNA established that the efficiency of the interaction was lowest for dimethyl sulphate and highest for MNU. This can apparently be explained by the fact that in the case of MNU and ENU the reaction intermediate is the alkanediazonium cation, which interacts electrostatically with DNA.[58]

The possibility of the carbamoylation of the DNA molecule in the reaction with MNU was first demonstrated[59] with the aid of tracer atoms. A DNA solution was treated for 72 h with MNU labelled at the carbonyl carbon atom with subsequent removal of the excess MNU (the ratio of the MNU and DNA phosphorus concentrations was 100 : 1).

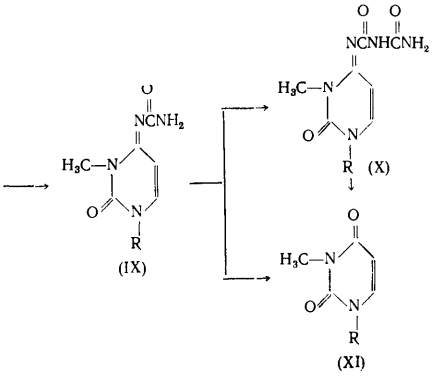
The hydrolysis of the modified [^{14}C]DNA to a depurinated acid with subsequent separation of the reaction products on ECTEOLA-cellulose demonstrated the presence of the label

in the depurinated fragment. It was suggested that the label is located in the phosphate fragment of DNA and (or) in cytosine.

Parallel experiments with nucleosides, polynucleotides, RNA, and DNA [60-67] confirmed the possibility of the carbamoylation of the NH_2 group of cytosine. The overall scheme for the reaction of MNU with cytidine[60,61] can be represented as follows:



(VII)

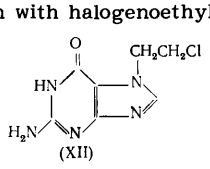


(IX) (X) (XI)

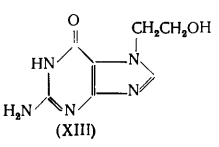
where R = ribose residue, (VII) = 4-*N*-carbamoylcytidine, (VIII) = 3-methylcytidine, (IX) = 3-methyl-4-*N*-carbamoylcytidine, (X) = 3-methyl-4-*N*-dicarbamoylcytidine, and (XI) = 3-methyluridine. Evidently the reaction of cytidine with MNU proceeds via two pathways—either via only carbamoylation to form compound (VII) or via alkylation with subsequent carbamoylation to form compounds (VIII), (IX), and (X). The carbamoylation products are readily hydrolysed with formation of compound (XI). On reaction with MNU, adenosine and guanosine give rise to carbamoylation products: 6-*N*-carbamoyladenosine, 1-methyl-6-*N*-carbamoyladenosine, and 2-*N*-carbamoylguanosine.[62]

The chloroalkyl derivatives of nitrosoureas have also been widely investigated.[68-71] Like MNU, these compounds decompose with formation of diazohydroxides, which alkylate the bases and phosphate groups of nucleic acid, and also isocyanates, which carbamoylate proteins, enzymes, and lipids.[72] Products of the interaction of ANU with nucleosides and DNA bases such as 7-chloroethylguanine (XII), 7-hydroxyethylguanine (XIII), 1,2-diguanylethane (XIV), 3-chloroethylcytosine (XV), and others have been identified.[73-76]

It has been established that the formation of DNA–protein and DNA–DNA cross-links, which have a significant influence on the cell metabolism, is possible in the reactions of chromatin with halogenoethylnitrosoureas:[71,76]



(XII)



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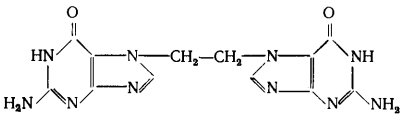

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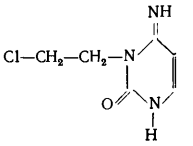

(XV)

IV. STRUCTURAL CHANGES IN DNA MODIFIED WITH ALKYLNITROSOUREAS

The chemical modification of DNA (alkylation, carbamoylation, etc.) can lead to significant changes in the DNA structure. Some of the damage can be made good by the operation of enzymes in the repair system. The irreparable structural defects alter the normal functioning of the cell genome.

The structural changes in the DNA molecule (single- and double-strand breaks, etc.) have been observed *in vitro* and *in vivo* by many investigators when DNA was treated with the usual alkylating compounds.[77-79] Alkylation of the bases can lead to the degradation of the DNA chains as a result of the removal of the purine, which leads to the rupture of the sugar–phosphate linkages in the molecule as a result of consecutive transformations in the DNA chain.[80-82] The alkylated phosphate groups of DNA (phosphotriesters) are formed on treatment with the majority of alkylating compounds. They are unstable in an alkaline medium, but their thermal stability is fairly high.[83]

In order to detect the chemical modification of DNA, one may use infrared (IR) spectroscopy, the application of which to nucleic acids and their components has been widely discussed in reviews and monographs.[84-87] It has been established that the IR spectra of films of DNA modified with MNU reveal a change in the intensities of a number of bands, although, overall, the form of the spectrum is altered only slightly.[30,88] Fig.1 illustrates the change in the intensities of a number of IR bands of DNA as a function of the time of its interaction with MNU. Evidently, the light absorption by a number of groups and bonds in DNA (with amino-groups and conjugated double bonds of the bases as well as the sugar–phosphate linkages) diminishes during the reaction, which shows that, in the course of the first 3 h of the reaction of MNU with DNA, there is a possibility of deamination, and the rupture of the double bonds of the bases and of the DNA chains, most probably as a consequence of the methylation and carbamoylation of the bases.

Combination of various methods of physicochemical and biochemical analysis[88-95] made it possible to identify and estimate quantitatively the principal types of the structural defects in DNA occurring under the influence of MNU. The numerical parameters defining the overall damage to the macromolecular structure [determined by the viscometric method after the thermal denaturation of DNA (10.4 ± 1.0) and by the kinetic formaldehyde method (the KF method)[88] (11.0 ± 1.0)] agree well with one another. The application of the methods involving neutral and alkaline electrophoresis in agarose gels and the enzymic treatment of the modified DNA with endonuclease S_1,[92,96] which is specific to the single-stranded sections of DNA,[93,94] made it possible to determine the ratios of the numbers of double-strand breaks (DB), single-strand breaks (SB), the alkali-labile sections (ALS), and the thermolabile sections (TLS).[89]

Data obtained by pulse polarography are consistent with the above finding.[91] It has been shown that a much greater number of SB are formed in DNA treated with MNU after thermal denaturation than after brief treatment with alkali.

The thermolabile sections apparently contain alkylated nucleotides, whose glycosidic and phosphoester linkages are weakened on raising the temperature.[97]

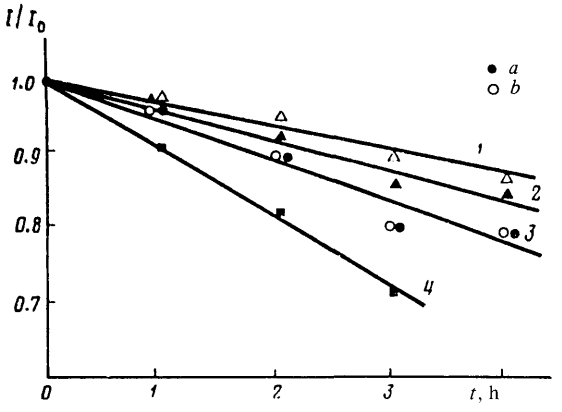

Figure 1. Dependence of the ratios of the intensities of a number of infrared bands of the modified DNA to the intensities of the infrared bands of native DNA on the duration of the interaction between DNA and MNU: 1) 960 cm^{-1} (vibrations of the sugar–phosphate linkages); 2) 1605 cm^{-1} (vibrations of the amino-groups of the bases); 3) 3350 cm^{-1} (*a*) and 3200 cm^{-1} (*b*) (vibrations of the amino-groups of the bases); 4) 1580 cm^{-1} (vibrations of the conjugated double bonds of the bases).[30]

The overall damage to the hydrogen bonds in the modified DNA can be estimated by two independent methods: from the decrease of the "melting" point on DNA T_m (the temperature of the transition of DNA from the helical to the disordered structure corresponding to the point of inflection on the curve relating the optical densities of the DNA solutions to temperature) and from the amount of the acid-soluble fragments (ASF) leached by nuclease S_1 from the modified DNA.[90]

Fig. 2*a* presents curves relating the optical densities of the DNA solutions to temperature for the control DNA (curve *1*) and after treatment with MNU for 4 h (curve *2*) and 16 h (curve *3*). Evidently T_m decreases during the reaction of DNA with MNU, which indicates an increase of the number of damaged hydrogen bonds in the modified DNA. This is also indicated by the increase of the amount ASF (Fig. 2*b*, curve *1*) in the reaction of DNA with MNU. The parallel increase of the relative amount of ASF with increasing difference between the T_m for DNA before and after its interaction with MNU (δT_m) (Fig. 2*b*, curve *2*) indicates a correspondence between the overall amount of sections with damaged pairing of the bases (which are converted by nuclease S_1 into the acid-soluble fraction) and the decrease of T_m, the quantitative relation (a decrease of T_m by 1° corresponds on average to 1% of damaged hydrogen bonds) being consistent with the data of Pritchard and Eichinger.[98]

It is noteworthy that the number of damaged hydrogen bonds is always greater than the number of alkylated bases and breaks produced. Thus, after 1 h of the reaction between MNU and DNA, the total damage to hydrogen bonds amounts to 2.5%,[90] while according to other data[53,99] the amount of alkylated DNA bases produced during the same period under identical conditions is 0.2–0.5%. Taking into account these data, the occurrence of the observed damage can be represented as follows.[100] Alkylation of different bases in the DNA molecule leads to the rupture of hydrogen bonds. The subsequent formation of depurinated sections also damages the hydrogen bonds. This leads to the formation of SB, which, as a result of statistical accumulation, can give rise to DB when they are close to one another. This pathway to the formation of SB can be accelerated by treating the modified DNA with alkali or by heating. According to Verly at al.,[95] 90 min heating at 100 °C is sufficient for the virtually complete removal of alkylated purines.

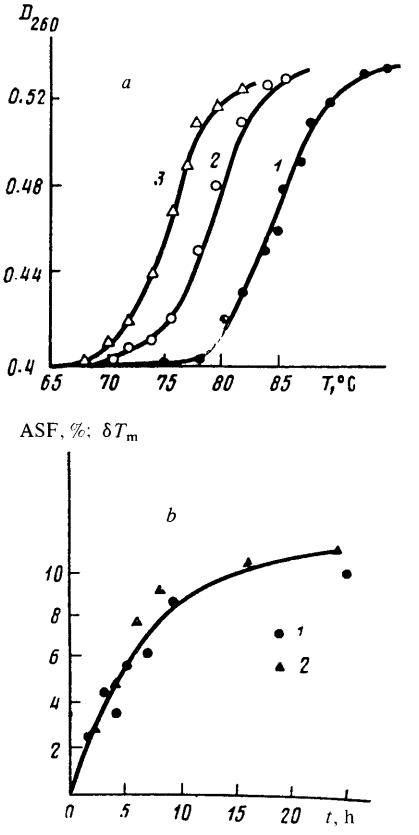

Figure 2. Melting curves relating the optical densities of the DNA solutions to temperature: 1) for native DNA; 2) after reaction with MNU for 4 h; 3) after reaction with MNU for 16 h; b) kinetic curves for the increase of the percentage content of the acid soluble fragments (ASF, curve *1*) and of the difference between the T_m of DNA before and after interaction with MNU (δT_m, curve *2*) in the reaction of DNA with MNU.[90]

The amount of sections where DNA has lost its helical structure as a result of alkylation (and other modifications) can be determined by the KF method,[101,102] which is based on the interaction of formaldehyde with the amino- and imino-groups of the DNA bases (not involved in the formation of hydrogen bonds) at temperatures below the "melting" point of DNA. This method has been used successfully to

observe the defects in the secondary DNA structure caused by the action of nucleases,[103] ionising radiation,[104] and thermal denaturation[105] and also to discover defects in the secondary structure of DNA in tumour cells.[106–108] The employment of the KF method for the analysis of the defects in the secondary structure of DNA produced in the reaction with MNU established that sections in which the DNA locally loses its helical structure are formed in the modified DNA and that their number agrees well with the number of SB determined by other methods.[89]

It has been established that the reaction of MNU with the tumour cell DNA is rapid[88,89] owing to the presence of sections in which the tumour cell DNA has locally lost its helical structure.[106–108]

V. BIOLOGICAL CONSEQUENCES OF THE CHEMICAL MODIFICATION OF DNA

The majority of the alkylated products detected in the reaction of DNA with MNU under *in vitro* conditions are also found under *in vivo* conditions.[109–111] As shown above, the main bulk of the alkylated products (up to 80% of the total amount) consists of 7-alkylguanine; adenine, guanine, cytosine, and thymine derivatives have also been detected. However, from the standpoint of mutagenesis and carcinogenesis, the greatest interest attaches to 6-*O*-alkylguanine and other oxygen-alkylated products.[110,112–114] In the course of the reactions of the alkylated products *in vitro* and *in vivo*, various intermediates can be produced, which alters significantly the mutagenic and carcinogenic activities of ANU and this must be taken into account when ANU are employed in experiments on living systems.[115,116] Mutations due to the alkylation of the DNA bases can arise as a result of erroneous base pairing. For example, when 6-*O*-alkylguanine is formed, the latter can pair with thymine (whereas under normal conditions thymine forms an A–T pair with adenine).[7,9,117–119]

As a result of the development of new methods for the identification of alkylated products, in recent years it has become possible to analyse the relation between the formation of these products and various manifestations of their biological properties.[120,121] A relation between the ability to alkylate guanine at the oxygen atom attached to the C(6) atom and the carcinogenic activity of the compounds has been established for many alkylating compounds;[122] however, the relation between the overall degree of alkylation and the carcinogenic activity was weak or almost altogether absent.[123] Alkylating agents [*N*-methyl-*N'*-nitro-*N*-nitrosoguanidine (NG) and methyl methanesulphonate (MMS)] produce similar types of damage in DNA. When a combination of NG and MMS was used to investigate the different types of damage leading to mutations, transformation, and toxicity, it was shown that the frequency of mutations is correlated with the number of methylated adducts of 6-*O*-alkylguanines, but the cytotoxicity is not correlated either with the number of individual adducts or with the total level of alkylation of DNA (NG is more than 100 times more toxic than MMS).[124]

Comparison of the carcinogenic activities of the alkylating compounds (*N*-methyl-*N*-nitrosourethane, MNU, ENU, NG, MMS, etc.) in experiments on rodents with the mutagenic effects of these substances on bacteria established that the alkylating activity is fully correlated with the mutagenic effect but there is no correlation between each of these effects and the carcinogenic activity. A relation has been observed between the initial ratio of the 7-*N*- and 6-*O*-alkylguanines formed as a result of the reaction of the alkylating compound with DNA *in vitro* and its carcinogenic activity *in vivo*. This is evidence that the alkylation of guanine in the 6-*O*-position plays a key role in damaging DNA and is responsible for the experimentally observed carcinogenic activity of the alkylating compounds.[4,114]

The malignant transformation of cells depends on the duration of the existence of the modified base in DNA, which in the case of 6-*O*-methylguanine proved to be longest for brain cells, which are the most sensitive to MNU. On the other hand, its removal from the liver DNA is much faster and liver proved to be resistant to the malignancy-inducing activity of MNU.[125–127] Thus alkylation of DNA may be one of the principal reactions in carcinogenesis and in the mutagenic action of chemical compounds, which themselves (or their reaction products) can add to the nucleophilic centres of DNA.[128,129]

The carbamoylation reaction, which is characteristic of ANU, makes it possible in many instances to account for the high mutagenic and antitumour effects of such compounds by the formation of carbamoyl derivatives. Thus, mutations can occur due to the products of the carbamoylation of the bases by isocyanic acid, since it has been shown that when many plants are treated with its salt (potassium isocyanate), mutant forms are obtained.[130] However, one should note that a clear-cut correlation has not been observed between the degree of carbamoylation of nucleic acids and the antitumour activity of ANU, although such correlation has been traced between the alkylating activity (for the same degree of carbamoylation) and the antitumour activity.[131]

It has been shown that the carbamoylation reactions can significantly inhibit the cell repair processes. The enzymes involved in the repair and replication of DNA can be inactivated as a result of carbamoylation by the isocyanates arising during the reaction with ANU.[70,71,132]

The protein carbamoylation reaction has assumed a definite importance as one of the possible explanations of the antitumour properties of ANU.[133,134]

The manifestation of the biological activity of ANU can be influenced significantly by the reactions of the alkylated products involving damage to the structural integrity of DNA (SB, DB, ALS, and TLS) and of the carbamoylated products (modification of proteins) and also by the formation of DNA–protein and DNA–DNA cross-links which have been detected with mammalian cells were treated with chloro-derivatives of ANU.[135,136] Experiments with bacterial cells established a correlation between the number of DB induced in DNA by MNU and the survival rate of the cells.[137] The destruction of cells under the influence of ANU may be also caused by the formation of a considerable amount of ALS, as happens when cells are exposed to ionising radiation.[138]

In many instances a definite relation has been discovered *in vivo* between the induction of breaks in DNA and the carcinogenic activity for a specific class of substances. However, one should bear in mind that single-strand breaks in cell DNA can arise additionally owing to the action of excision reparation enzymes, which are capable, for example, of excising 3-alkyladenine and 6-*O*-methylguanine with formation of a depurinated section, which subsequently gives rise to SB.[131,139]

The alkylation and carbamoylation reactions, accompanied by a significant damage to the DNA structure, can alter the template properties of the latter which are responsible for the replication and transcription process.[140]

A very sensitive test of the template properties of the modified DNA may be provided by RNA polymerase systems of purified nuclei and with a soluble RNA polymerase.[141–143] The interference with the synthesis of RNA using as a template DNA modified with MNU has been investigated.[144,145] The template activity was determined from the amount of

[^{14}C]CMP in the RNA produced relative to the control (Fig.3, curve *1*). The control consisted of a system with untreated DNA. Evidently, even during the first hours of the reaction, the template activity diminishes exponentially. The extent of the disturbance of the template activity was greater the longer was the reaction between MNU and DNA. After 10 h, there is virtually no synthesis of RNA. Comparison of these results with the appearance of SB and DB in the DNA molecule under the influence of MNU (Fig.3, curves *2* and *3*) demonstrates a greater sensitivity of the RNA polymerase system to the damage sustained by the DNA structure than is shown by other methods. The cessation of template synthesis after 10 h indicates a significant damage to the DNA template, leading to the inhibition of transcription.

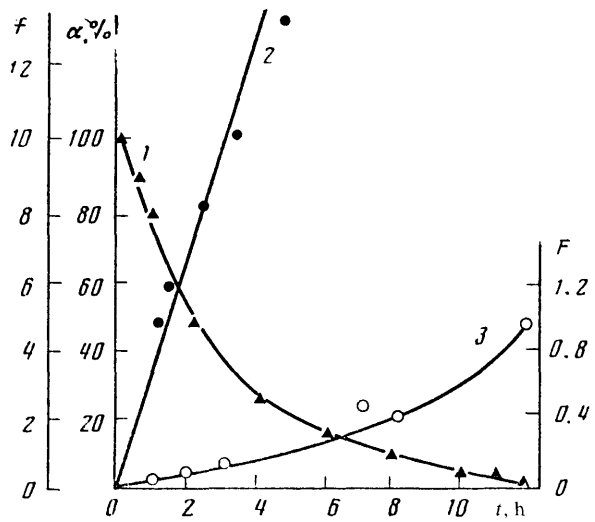

Figure 3. Variation of the template activity of DNA in the RNA polymerase system (curve *1*) {determined from the degree of incorporation α of [^{14}C]CMP in the RNA produced} and of the numbers of SB (*f*, curve *2*) and DB (*F*, curve *3*) as a function of the duration of the interaction of DNA with MNU.[143]

The change in the template properties of chromatin under the influence of MNU and the chloroethyl derivatives of nitrosoureas has been established[146] and in many instances the degree of inhibition of the template activity was found to be correlated with the antitumour effect of the ANU.

It has been established that ANU exhibit an antitumour activity with respect to malignant neoplasts of different origin and those induced by carcinogens in animals. However, the question of which of the DNA modification reactions is decisive in the manifestation of the antitumour activity of ANU is at present still obscure. It is assumed that the greater degree of inhibition of the DNA synthesis in tumour cells plays a significant role in this process owing to the decrease of the template activity of chromatin (as a result of alkylation and carbamoylation) and also the inhibition of the tumour cell reparation processes (resulting from the carbamoylation of the enzymes).[70] One cannot rule out the possibility that the selectivity of the action of ANU on tumour cells is based on their reactions with DNA whose structure differs from the DNA of the normal cells by the presence of sections in which the molecules have locally lost their helical structure,[106-108], which is responsible for the greater sensitivity of the tumour DNA to the action of chemical[100,147] and physical[148] agents.

Thus analysis of the possible ways of modifying DNA by alkylating compounds, particularly by ANU, makes it possible to relate the observed biological effects to different types of damage to the primary and secondary DNA structures and also to estimate the possibility of the specific synthesis and application of new biologically active preparations.

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The Peroxide Oxidation of Membrane Lipids and Natural Antioxidants

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The ways in which membrane lipids are oxidised are considered and the initiating and protective systems influencing the rate of this process are classified. The regulatory role of the interrelation between the composition of the membrane lipids and the degree of their oxidation, which makes it possible to regard this process as a procedure for the rapid renewal of the composition of the lipids and the alteration of the functional activity of membranes, is discussed. The kinetic characteristics of natural antioxidants as radical process inhibitors are presented and the characteristic features of their activity are deduced. They are discussed in terms of their involvement in the regulation of the peroxide oxidation of lipids.
The bibliography includes 119 references.

CONTENTS

I. Introduction 907
II. Systems regulating the rate of the peroxide oxidation of membrane lipids 907
III. The composition of lipids and the intensity of their oxidation 911
IV. Natural antioxidants 911

I. INTRODUCTION

The research into the peroxide oxidation of lipids (POL) in the USSR was initiated by studies carried out in 1954–1956 in Moscow State University and at the Institute of Chemical Physics at the USSR Academy of Sciences, which have been recognised as giving priority in this field to the Soviet Union.[1,2]

At the present time this field has been developing successfully not only in the USSR but also abroad. It is not fortuitous that so much attention has been devoted to the question of the biological significance of the oxidative processes occurring in membrane lipids. It has been established that the accumulation of the lipid oxidation products in membranes alters the structure of the latter and their functional activity. Lipid peroxides, which are the primary and labile lipid oxidation products, have attracted most attention by investigators.

The peroxide oxidation of lipids has been regarded for a fairly long time by many investigators as an undesirable process, which is actually harmful for the organism. This was promoted by the establishment of the following facts: (1) peroxides have been detected most frequently in the organs of animals following the development of various pathological conditions; (2) it has been shown in many studies that the administration of oxidised lipids to animals is toxic for the organism;[3,4] (3) the appearance of peroxy-groups in the aliphatic acid residues of membrane phospholipids alters the properties of the latter such as permeability and the stability of the lipid–protein complexes and induces the inactivation of enzymes.[5-11]

Questions associated with the role of natural antioxidants in the regulation of the peroxide oxidation of lipids are examined in this review.

II. SYSTEMS REGULATING THE RATE OF THE PEROXIDE OXIDATION OF MEMBRANE LIPIDS

The discovery in 1963[12] of two pathways leading to the peroxide oxidation of lipids, namely enzymic and non-enzymic, and the vigorous investigation of these processes in recent years have altered somewhat the assessment of the biological role of peroxides.

Many factors proved to be important for the establishment of the hypothesis of a significant role of peroxide oxidation for normal metabolism.

1. The improvement and increase of the sensitivity of methods for the determination of peroxides made it possible to detect them in many organs and tissues of intact animals.

2. Enzyme systems regulating both the rate of formation of peroxides and the rate of their utilisation have been discovered and investigated.[13-18] This means that peroxide formation and utilisation processes are characteristic of norma metabolising cells and the amount of peroxide in the membrane must be maintained at a specific stationary level.

3. Careful investigation of the toxicity of oxidised lipids showed that not so much the peroxides as the products of the more far-reaching oxidation of lipids, namely aldehydes, ketones, and acids, are toxic for the organism.[19]

4. It has been shown that lipid peroxides are intermediates employed by the organism for the synthesis of biologically active substances: prostaglandins, thromboxanes, steroid hormones, etc.[20-23] and they cannot therefore be regarded as undesirable side products of the oxidation process.

The synthesis of these substances in the organism from unsaturated aliphatic acids is achieved in several stages via the formation of short-lived labile endoperoxides under the influence of specific enzymes. For example, the cyclisation of arachidonic acid entails the formation of endoperoxides (the prostaglandins G_2 and H_2), which are transformed into the prostaglandins E_2, D_2, and $F_{2\alpha}$. When the thromboxane synthetase, localised in the membranes of thrombocyte microsomes, acts on the endoperoxides in this case, the thromboxanes A_2 and B_2—substances with pronounced adhesive properties, are formed. When the endoperoxides are acted upon by the enzymes of the microsomal fraction of the arteria vessels, the biosynthesis is switched towards the formation of prostacyclin—a substance which possesses antiadhesive and deaggregating activity, several tens of times superior to the antithrombic activity of prostaglandins.[20] Consequently, depending on which enzyme system is involved in biosynthesis, biologically active substances with different,

sometimes directly opposed, properties are formed from the same precursor—the endoperoxide of arachidonic acid. Peroxides are a universal raw material which is employed by the organism for a wide variety of purposes.

5. The peroxide oxidation of lipids is interrelated with the processes involving the renewal of the composition of the membrane phospholipids. It has been shown that an increase in the peroxide oxidation of lipids accelerates the metabolism of phospholipids, alters their relative composition, alters the lipid–protein ratios, and hence alters the structure of the membrane.[24–27]

The interrelation between the rate of the peroxide oxidation of lipids and the change in the composition of lipids is based on the acceleration of the release of phospholipids from membranes with increase of the rate of peroxide oxidation. In model experiments with isolated membranes a decrease of the phospholipid/protein ratio was observed after the induction of peroxide oxidation and a decrease of the relative amount of the readily oxidisable phospholipids such as phosphatidylethanolamine, phosphatidylserine, cardiolipin, and phosphatidylinositol. Acceleration of the "flip-flop" and the passive transfer of lipids has been demonstrated.[28,29] On the other hand, the data concerning active transport with the aid of lipid-transferring proteins are extremely contradictory. Thus it has been observed[29] that the induction of peroxide oxidation does not influence or even suppresses the transfer of phosphatidylcholine between membranes by the lipid-transferring protein.

Data concerning the role of the fluidity of lipid membranes in the activity of lipid-transferring proteins have been published.[30,31] It has been shown that a rigid state of the lipid-donor membrane is the most favourable for the operation of the lipid-transferring proteins. Since lipid peroxides increase the microviscosity of the lipid double layer in membranes,[32] they can thus increase the activity of the lipid-transferring proteins and the rate of release of lipids from the membrane.

One should bear in mind also the acceleration of the cleavage of the oxidised phospholipids with the aid of phospholipases compared with the unoxidised phospholipids.[33] Experiments *in vivo* showed in all the cases investigated that an increase in the peroxide oxidation enriches the lipid membranes in fractions more resistant to oxidation (phosphatidylcholine, sphinogomyelin, and cholesterol).[34–36] The results, which are treated from the standpoint of the alteration of the rate of catabolism of the phospholipids, have been confirmed by the alteration of the turnover times of the membrane lipids. This has been effectively demonstrated for irradiated plant cells.[36,37]

Calculations have shown that the turnover times for readily oxidisable phospholipids are satisfactorily consistent with the rate of their peroxide oxidation, which makes it possible to regard the peroxide oxidation of lipids as one of the important factors responsible for the renewal of the membrane lipids.

Numerous studies demonstrating the lipid-dependence of the membrane proteins, namely enzymes, receptors, channel-forming agents, translocators, etc., have been published recently. The change in the composition of lipids induced by the change in the rate of peroxide oxidation therefore alters also the activity of these membrane proteins.

6. It has been shown that the lipid peroxides themselves can both activate and inhibit the activity of enzymes[38–40] and can also play the role of allosteric effectors. The interactions of lipid peroxides with the catalytic and allosteric centres of proteins justify the differentiation from the lipid-dependent enzymes of a separate group of peroxylipid-dependent enzymes.[38,41,42]

An important factor in the action of lipid peroxides on enzymes is the possibility that they may transform the enzyme activity.[41]

Thus all these data support the view that the peroxide oxidation of lipids should be regarded as a physiological process and the lipid peroxides as the products of the metabolism of the normal metabolising cells. The low level of lipid peroxides characteristic of normal tissues by no means implies that peroxide oxidation does not occur in such tissues and can be explained by the fact that the processes involving the formation and consumption of peroxides are well balanced and that lipids are oxidised at a specific stationary level.[43]

On development of pathological states, such balance can be disturbed, the peroxides formed accumulate in the tissues and lead to serious damage to the bio-membranes.

We shall consider how a stationary lipid oxidation level is maintained in membranes. The oxidation of membrane lipids is a complex multistage process with its own characteristic features determined primarily by the involvement in the oxidation reaction of a number of enzymes, the structural organisation of the lipid double layer in the membranes, the high degree of unsaturation of the aliphatic acids forming part of the composition of the phospholipids, the multicomponent composition of the lipids, and the presence in the latter of substances capable of intensifying or weakening the effect of natural antioxidants and initiating oxidation.

It is noteworthy that only the enzymic pathway to the peroxide oxidation of lipids is at present recognised as a normal physiological process. The non-enzymic pathway to the autoxidation of lipids is still regarded by many investigators as an uncontrolled process, which is therefore abnormal. We believe that this view is incorrect.

The autoxidation of lipids is a special case of the liquid-phase oxidation of hydrocarbons whose theoretical principles have been examined in detail by Emanuel's school[44–49] and which constitutes a typical chain process with degenerate branching. A distinctive feature of such processes is an extremely high sensitivity to very slight changes in the composition and proportions of the components of the oxidation reaction and in the concentrations of various additives which can play the role of oxidation inhibitors or activators. These properties are in fact important for processes involved in the regulation of the functional activity of membranes. In contrast to oxidation *in vitro*, the rate of which can be varied appreciably within wide limits by altering the temperature, composition, and the component ratios, in membranes such changes are possible only within very restricted limits. Only processes whose rate depend significantly on slight changes in the composition of the components can therefore fulfill a regulatory function. Such requirements are met most fully by degenerate-branched chain oxidation processes. The non-enzymic oxidation of lipids can therefore hardly be regarded as an avalanche-like uncontrollable process. The question whether non-enzymic oxidation can take place in the lipid double layer in membranes in which the aliphatic acid residues of the phospholipids have a structural organisation is still controversial. However, the recognition of a mosaic structure of membranes with "lipid seas" permits the assumption that all the conditions necessary for the homogeneous liquid-phase oxidation are fulfilled in the oxidation of lipids.

The properties of lipids as oxidation substrates to some extent resemble those of polymers by virtue of the high degree of structural organisation in the lipid double layer in membranes. It has been shown that the characteristics deduced for the liquid-phase oxidation of organic substances can be legitimately applied to the low-temperature oxidation of polymers.[50] On this basis, one can assume that all the

features of the oxidation of lipids established in model systems will be manifested also in the oxidation of membrane lipids, although undoubtedly the structure of biological membranes should exert a significant influence on the intensity of this process.

Thus one may postulate that the oxidation of lipids in membranes can also take place via a non-enzymic mechanism. The question arises whether it is necessary to draw a sharp boundary between these two lipid oxidation pathways. It is noteworthy that the two lipid oxidation pathways have much in common, although they differ as regards the mode of initiation and the set of intermediate and final oxidation products.

In both cases the oxidation of lipids proceeds via a stage involving the formation of lipid free radicals which are fairly active and long-lived. The rate of oxidation depends significantly on the composition of the membrane phospholipids, especially on the number of double bonds in the unsaturated aliphatic acids (UAA), on the degree of structure formation in the lipid phase of the membrane, and on the presence of inhibitors, activators, and other substances which are highly effective even at low concentrations. In all probability the oxidation pathways at different stages can merge. Thus the active forms of oxygen produced enzymically can initiate the non-enzymic oxidation.[51-53] On the other hand, glutathione peroxidase decomposes lipid peroxides regardless of the pathway (enzymic or otherwise) which led to their formation.[54-57]

Regardless of whether the lipids are oxidised non-enzymically or with participation of enzymes, the following principal elementary stages in the development of this process must be considered: initiation, propagation, branching, and termination of the oxidation chains (Scheme 1):[44-49]

Scheme 1

$$\left.\begin{array}{l} RH \xrightarrow{k_1} R^{\cdot} \\ R^{\cdot} + O_2 \xrightarrow{k_2} RO_2^{\cdot} \end{array}\right\} \text{chain initiation;} \quad (0), (1)$$

$$RO_2^{\cdot} + RH \xrightarrow{k_3} ROOH + R^{\cdot} \quad \text{chain propagation;} \quad (2)$$

$$ROOH \xrightarrow{k_4} RO^{\cdot} + HO^{\cdot} \quad \text{chain branching} \quad (3)$$

$$\left.\begin{array}{l} R^{\cdot} + R \xrightarrow{k_5} \text{molecular products} \\ RO_2^{\cdot} + R^{\cdot} \xrightarrow{k_6} \text{molecular products} \\ RO_2^{\cdot} + RO_2^{\cdot} \xrightarrow{k_7} \text{molecular products} \end{array}\right\} \text{chain termination;} \quad (4), (5), (6)$$

RH = oxidation substrate.

The overall rate of oxidation of membrane lipids is determined by the ratios of the rates of each of these stages. A change in the rate of any oxidation stage leads to the breakdown of the steady-state nature of the process, to a change in the overall rate of oxidation, and to the accumulation of lipid peroxides in membranes, which can in its turn entail the appearance of states which are not characteristic of the normal cell. We believe that there exist several initiating and protective systems in the cell which alter the rate of oxidation of lipids and which can be regarded as regulatory. These systems can be divided into four groups.[43]

System I is responsible for a rigorously defined structural organisation of lipids and thus influences the rate of the chain initiation, propagation, and termination reactions.

System II comprises enzymes responsible for the formation and destruction of the active forms of oxygen and free radicals initiating the oxidation process and the enzymes participating in the decomposition of peroxides without the formation of free radicals from the latter.

System III regulates the metabolism of the membrane phospholipids and influences the rate of oxidation by altering the composition of the phospholipid UAA, the ratios lipid/protein, phospholipids/cholesterol, etc.

System IV comprises low-molecular-weight substances which fulfill the role of initiators, catalysts, inhibitors, quenching agents, synergistic agents, etc. and which influence the chain branching and termination stages.

It is already possible to state that the operations of these systems are inter-related and that the principal role cannot be attributed to any of them: each system operates within rigorously specified limits and in different cases the dominant and rate-limiting reactions change. It is therefore undesirable to speak of the first or second line of defence, as has been done in Fridovich's studies.[14,17,18]

We shall consider briefly the operation of these systems in different stages of the oxidation process.

The Chain Initiation and Propagation Stage. The steady-state concentration of lipid peroxy-radicals is determined by the composition of the lipid UAA (the strength of the double bonds), the concentrations of substances capable of rupturing the double bonds, and the rate of destruction of lipid peroxy-radicals. It is now known that several types of free radicals, differing both in the way they are formed and in their activity, exist in the cell. We shall not consider the primary mechanism of the generation of free radicals in membranes, because a whole series of reviews have been devoted to these questions.[18,51,57,58] We shall only note that, regardless of the nature of the free radicals formed, on the basis of the principle of the indestructibility of the free valence, they are exchanged for the lipid peroxy-radicals and the rate of this exchange is fairly high. An increase in the concentration of the lipid peroxy-radicals in membranes leads to an increase of the overall rate of oxidation, which is proportional to their concentration. It must be specially emphasised that we are considering only short-lived lipid peroxy-radicals. A change in the concentration of lipid peroxy-radicals, their additional formation or destruction caused by a change in the rate of operation of particular systems, leads to a change in the steady-state nature of the process.

Systems influencing the conditions governing the formation of active radicals in membrane lipids will therefore alter also the overall rate of oxidation. In all probability, the structural organisation of membrane lipids (system I), which influences the accessibility of the membrane phospholipid UAA to the action of oxygen, plays a decisive role in this instance. The closer the packing of the UAA in the membrane phospholipids, the smaller their accessibility to O_2 or singlet oxygen (O_2^*), and the lower the rate of initiation of free radicals. Any agents which interfere with the packing of the UAA (for example, chaotropic agents) accelerate the oxidation of lipids. Factors which maintain the membrane lipid structure inhibit oxidation.

Substances capable of deactivating O_2^* (singlet oxygen quenching agents) also alter the rate of initiation and inhibit the overall rate of oxidation (System IV).

A change in the activity of the enzymes involved in the formation or destruction of free radicals and the active forms of oxygen (system II) also exerts a major influence on the overall rate of oxidation of lipids. The activity of such enzymes depends on the degree of structural organisation in the lipid double layer in the membranes.

Indeed, it has been shown, for example, that the activity of the enzymes responsible for the formation of peroxy-radicals requires the lipids be in a liquid state, an increase in viscosity resulting in the inhibition of these enzymes.[56,59]

At the same time, in the non-enzymic generation of free radicals, the rate of initiation is also greatly influenced by a change in the viscosity of the lipid component. The liberation of radicals from the cage is significantly inhibited with increase of the viscosity.[60,61]

Attention should be drawn to the fact that in a normal metabolising cell, whose membranes have not been significantly changed, the degree of structural organisation in the lipids in all probability changes within restricted limits. When the peroxide oxidation of lipids in membranes is modelled by *in vitro* experiments, the structural organisation in the lipid double layer is disturbed. Therefore, the quantitative characteristics obtained in such model systems can be transferred, but with some caution, to the *in vivo* oxidation of lipids, the degree of structural organisation of which has a decisive influence on the rate of their oxidation.

Certain vitamins with long-chain side groups (system IV) are able to stabilise membrane lipids by improving the structural organisation of the lipid double layer. Recently the hypothesis of a structural interaction of tocopherols with components of biological membranes has gained wide currency.[62-64] According to the concept of these authors, the tocopherol molecule stabilises the membrane as a result of the specific interaction between its phytyl side group and the aliphatic acid chains of the membrane phospholipids. This model presupposes the interaction between the methyl groups of the side chains in tocopherols and the *cis*-double bonds of the UAA in such a way that the CH_3 group at the C(4) and C(8) atoms of the tocopherol side chain enters the "pockets" formed by the double bonds of the UAA residues of the phospholipids. The interaction takes place via van der Waals forces and increases the packing density of the membrane phospholipids, which hinders the penetration of oxygen to the UAA double bonds and the formation of lipid peroxy-radicals and entails a decrease of the overall rate of oxidation.

Vitamins with a different structure, which give rise to intermediate radical species in the oxidation reactions (vitamins A, C, D, and F) at certain concentrations, can play the role of initiators and can accelerate the oxidation of lipids by increasing the rate of formation of free radicals.[13,65-68] Variable valence metal ions, particularly the Fe^{2+} and Cu^{2+} ions[7,9,69] (system IV) can play a similar role of initiators. The rate of propagation of the oxidation chain depends significantly on the composition of the UAA of the phospholipids and on the degree of their saturation. For this reason, the changes in the metabolic rate of phospholipids and in the rate of their emergence from the membranes alter also the overall rate of oxidation (system III).

Thus the overall rate of oxidation of lipids at the chain initiation and propagation stages depends on all four systems: on the change in the structural organisation of the membrane lipids (system I and IV); on the activity of the enzyme system involved in the formation and destruction of free radicals and active forms of oxygen (system II); on the presence of singlet oxygen quenching agents (system IV); on the composition of the phospholipid UAA (system III); on the presence in the lipid of substances playing the role of oxidation initiators (system IV).

The Chain Branching Stage. The primary products of the oxidation of lipids are hydroperoxides, which are fairly labile and are capable of spontaneous decomposition into free radicals, which makes it possible to regard the oxidation of lipids as a degenerate-branched chain process. The rate of the chain branching reaction is determined both by the stability of the hydroperoxides formed and their amount. The stability of the hydroperoxides depends in its turn primarily on the structure of the UAA. The factors which alter the aliphatic acid composition of the membrane phospholipids (system III) therefore alter not only the susceptibility of these lipids to oxidation but also the stability of the hydroperoxides formed. The steady-state amount of peroxides in the lipid double layer depends both on the rate of their formation and on the rate of their release from the membranes.

Enzymes utilising ROOH (system II) therefore diminish their amount and hence the rate of the chain branching reaction and the overall rate of oxidation (for example, glutathione peroxidase, catalase, peroxidase).[14-17,69,70] Mercapto-compounds, which decompose peroxides via a molecular pathway without the formation of free radicals, have the same effect on the overall rate of oxidation (system IV).[71] Variable-valence metal ions, especially Fe^{2+} ions at low concentrations, catalyse the decomposition of peroxides into free radicals and thereby increase the overall rate of oxidation.[69]

Thus the overall rate of oxidation in the chain branching stage depends directly on the operation of three systems: on the activity of the enzyme system regulating the metabolism of membrane phospholipids (system III); on the activity of the enzyme system utilising hydroperoxides without the formation of free radicals (system II); on the presence in lipids of phosphorus- and sulphur-containing substances, which decompose peroxides without the formation of free radicals, and on the concentration of variable valence metal ions (system IV).

As regards the involvement of system I in the regulation of the rate of chain branching, its influence operates via other systems (systems II and III). As already stated, the effective lipid transfer between membranes, the catabolism of the oxidised forms of the lipids, and the operation of a number of enzymes of system II depend on the viscosity of the lipid. Nor is it possible to eliminate the influence of the viscosity of the medium on the [rate?] constant for the decomposition of peroxides into radicals. However, we were unable to find in the literature any special studies devoted to these questions.

The Chain Termination Stage. This stage consists of reactions involving the quadratic termination of peroxy- or alkyl-radicals derived from lipids (their recombination or disproportionation) and linear termination reactions at the interface or in the bulk phase, for example, linear termination by the molecules of natural antioxidants.

The change in the composition of peroxy-radicals resulting from the change in the composition of phospholipids (system III) can alter the rate of their recombination, the steady-state concentration of peroxy-radicals, and ultimately also the overall rate of oxidation of lipids. A change in the concentration of substances whose molecules are responsible for linear chain termination (system IV) alters markedly the overall rate of oxidation of lipids.

It must be specially emphasised that only natural antioxidants (AO) possess the ability to react directly with lipid peroxy-radicals. If an additional amount of free radicals are formed as a result of some kind influence on membrane lipids, whose generation could not be prevented either by the structural (system I) or enzymic (system II) protective systems, then the exchange reaction of these radicals with the lipid substrate can result in their exchange with the lipid peroxy-radicals. The excess concentration of lipid peroxy-radicals can be abolished only by natural antioxidants and their influence on the overall rate of oxidation greatly exceeds the effectiveness of the action of other systems. This is the reason for the special role of natural antioxidants in the regulation of lipid peroxide oxidation processes.[5]

Thus the overall rate of oxidation of lipids in the chain termination stage depends on the change in the UAA composition in the phospholipid metabolism (system III) and on the activity of the system of natural antioxidants and their synergists (system IV).

The principal features of the operation of systems III and IV have been analysed within the framework of this review. The characteristics of the operation of systems I and II are not considered in detail because the literature contains a number of detailed reviews on this topic.[15,18,57,72,73]

III. THE COMPOSITION OF LIPIDS AND THE INTENSITY OF THEIR OXIDATION

The present stage of the investigation of the characteristic features of the peroxide oxidation of lipids is characterised by an increased interest in kinetic studies in terms of the comparative aspects of the oxidation of individual phospholipids as well as phospholipids forming part of the composition of membranes by means of a series of models of increasing complexity. The models employed permit the elucidation of the role of fluidity, change, hydrophobic properties, and other physicochemical characteristics of the lipid double layer in the kinetics of peroxide oxidation.

Table 1. The influence of the medium on the kinetic characteristics of the initiated oxidation of lipid substrates of different composition.

Oxidation substrate	Yield of radicals	$10^3 k_2/\sqrt{k_6}$, litre$^{1/2}$ mol$^{-1/2}$ s$^{1/2}$	Refs.
Methyl oleate*	0.7	4.4	[76]
Methyl linoleate*	1.2	13	[76]
Methyl linolenate*	0.83	32	[76]
Cholesterol*	—	3.2	[77]
Phosphatidylcholine*	0.66	610	[78]
Phosphatidylcholine**	0.04	17.0	[78]

*Solution in chlorobenzene.
**Aqueous suspension.

Previously it was known that phospholipids whose composition includes unsaturated aliphatic acids are most readily oxidised. Studies in recent years have shown that the oxidation of phospholipids is influenced by the structure not only of the aliphatic acid residues but also by that of other components. Thus in a study of the oxidation of phosphatidylcholine (PC) and phosphatidylethanolamine (PEA), which have identical aliphatic acid compositions, it was found that the latter lipid is oxidised faster.[75] One of the important questions concerning the kinetics of the oxidation of phospholipids involves the study of the problem of the way in which the kinetic characteristics of the oxidation process vary in liposomes or micelles, compared with the oxidation of phospholipids in a homogeneous solution in an inert solvent. Table 1 presents the kinetic characteristics of the initiated oxidation reactions of the methyl esters of oleic, linoleic, and linolenic acids as well as cholesterol in benzene and of phosphatidylcholine in chlorobenzene and in the form of micelles.[76-78] Table 1 shows that the phosopholipid is oxidised significantly faster in a homogeneous medium (by a factor of 20) than the methyl esters of aliphatic acids and cholesterol. On passing to oxidation in the form of micelles, the yield of radicals diminishes sharply and the rate constant ratio $k_2/\sqrt{k_6}$ decreases by a factor of 35. According to Ingold,[78] changes in the viscosity and polarity of the medium exert the main influence on the rate of the chain propagation reaction [reaction (2)] in Scheme 1.

The high polarity of the peroxy-radical increases the possibility of its migration to the surface of the micelle, as a result of which the probability of recombination increases and the rate of the chain propagation reaction falls.

A further increase in the complexity of the model and its closer approach to the real conditions in the peroxide oxidation of lipids in cell membranes involves the study of the characteristic features of the oxidation reaction and of its inhibition in systems for the oxidation of mixtures of hydrocarbons. In the oxidation of two or several substrates, it is essential to take into account the occurrence of the so-called chain termination and propagation cross-reactions. Data for the kinetics of the co-oxidation of the methyl esters of aliphatic acids have been published.[79]

As a result of the co-oxidation, the same substrate can intensify the oxidation of slowly oxidised substrates and can inhibit that of rapidly oxidised substrates. Studies by the authors of this review revealed that the addition of PC to the rapidly oxidised microsomal lipids inhibits their oxidation, while its addition to slowly oxidised lipids intensifies it. Analogous data have been obtained for cholesterol and PEA.[80,81]

The next stage in the increase of complexity involves the study of the characteristics of reactions during which products functioning as inhibitors or initiators of the oxidation process are formed. Such substances include, in particular, cholesterol and PC.[80] The antioxidant activity of the products of the oxidation of such lipids has been demonstrated.[80,81]

The study of peroxide oxidation processes in a mixture of lipids made it necessary for investigators to take into account not only the change in the rate of initiation and the occurrence of chain propagation and termination cross-reactions, but also the changes in the charge, viscosity, and hydrophobic properties of the mixture. A change in the latter leads in its turn to an alteration of the elementary reaction constants and also of the activity of the enzyme initiating or inhibiting the peroxide oxidation of lipids. Thus complex changes in the inter-relations of the components of the regulatory systems III and IV take place during the oxidation process. In order to understand the characteristic features of the regulation of the peroxide oxidation of lipids by antioxidants, it is necessary to consider in greater detail their kinetic characteristics.

IV. NATURAL ANTIOXIDANTS

The natural antioxidants or bioantioxidants are substances of plant or animal origin which inhibit the development of oxidation processes in model reactions. It has been demonstrated for model oxidation reactions that the lipids isolated from various organs of intact animals (liver, spleen, brain, and blood) do indeed inhibit the development of oxidation processes.[5] The overall antiradical activity of the natural antioxidants contained in the lipids of the livers of intact animals, which has the high constant $k_7 = 2.0 \times 10^6$ litre mol^{-1} s^{-1}, has been determined by chemiluminescence[5] and the effective active fraction of the natural antioxidants, which amount to 0.3% of the total mass of lipids, has been calculated.

Cell bioantioxidants consist of exogenic antioxidants supplied with food and endogenic antioxidants which enter the cell by the humoral pathway or are synthesised in it.

Many experimental data show that the deficiency of particular natural antioxidants in the organism leads to the intensification of the oxidative processes in lipids and to the appearance in the latter of oxidation products in greater than normal amounts.

Various biologically active substances, namely tocopherols, ubiquinones, steroid hormones, etc., exhibit antioxidant activity in model experiments. It has been suggested that these substances fulfill the antioxidant function in the organism together with other functions specific to them.

The question of the contributions of various components of lipids to their antioxidant activity (AOA) has been widely discussed in the literature. However, there is no single point of view on this question. Some investigators attribute the antioxidant activity of lipids to the presence in them of an individual substance (for example, tocopherol or ubiquinone) others believe that the activity of lipids is determined by the set of properties of various components, a change in the composition of which is expressed by a change in the properties of lipids as a whole.[5] We believe that the AOA of lipids depends on the antioxidant properties of natural antioxidants, their amount, their possible mutual influence, and their interaction with substances which are not themselves antioxidants but increase or decrease the activity of the latter. In order to demonstrate the validity of a particular point of view, it is necessary to investigate the kinetic characteristics of natural antioxidants.

The structures of natural antioxidants have many features in common. Three groups of substances have the closest chemical structures: tocopherols, ubiquinones, and vitamins of group K.[82-87] On the basis of the similarity of the structures of these compounds and the interrelation of their metabolisms, it has been suggested that they can be interconverted in the organism. However, experiments involving the administration of 14C-labelled α-tocopheryl acetate showed that this hypothesis is incorrect.[110,119]

Each of these groups includes structurally related compounds: quinones, quinols, chromenols, and chromanols.[87] Quinols (hydroquinones) and cyclic chromenols and chromanols are reduced forms, while quinones are oxidised forms. In the course of many reactions occurring in lipids, intermediate forms such as epoxy-compounds, phenoxy-radicals, and semiquinone radical-anions can also be produced. In the organism, in the lipid double layer of the membrane, these forms can be interconverted and there exist enzymes which catalyse such interconversion. Each group of natural antioxidants is present in the lipids preferentially in one of the most stable forms for the given compound.

Thus vitamins of group K exist in blood in the form of quinones. Under the influence of dehydrogenase, the quinone gives rise to the hydroquinone form of vitamin K_1, which participates in the formation of prothrombin in the γ-glutamic acid carboxylation stage. Hydroquinone is then converted with the aid of epoxygenase into the epoxide of vitamin K_1, which is then converted by reductase into the oxidised quinone form.[88,89] The vitamin K isolated from lipids and converted into the hydroquinone form is extremely unstable, is readily oxidised in air, and loses its ability to react with peroxy-radicals.

The quinone form of ubiquinones is also the most stable. In the electron transport along the respiratory chain in the presence of reductants of the type of NAD, the quinone forms of ubiquinones are readily converted into the hydroquinone forms and conversely, with formation of semiquinone radicals. The hydroquinone form is fairly unstable and is oxidised to the quinone form by atmospheric oxygen. The cyclic forms of ubiquinones (ubichromenols) are the most stable. They are not involved in electron transfer along the respiratory chain. It has been suggested that these substances behave as antioxidants in lipids.[82,83,86]

Tocopherols are present in lipids mainly in the cyclic form as 6-hydroxychromans and this applies to both free tocopherol and its esters. In the organism the ester forms are readily hydrolysed to free tocopherol by enzymes.[90] In oxidative reactions, tocopherols, which function as antioxidants, react with peroxy-radicals to form phenoxy-radicals and these are then converted into quinones, dimers, and trimers.[91]

All the natural antioxidants belonging to the group considered have aliphatic substituents in the 2-position, which consist of several isopentane units. For ubiquinones, the number of isopentane units varies from 0 to 10 (from 0 to 50 carbon atoms), for vitamin K from 0 to 4 (up to 20 carbon atoms), and for the tocopherol homologues encountered in nature the number of units is always 3 and the phytyl side chain has 16 carbon atoms.

The side chains of natural antioxidants differ in the degree of unsaturation: there are no double bonds in the side substituents in tocopherols, in vitamins K the first isopentane unit is unsaturated, and each chain of ubiquinones contains one double bond in each isopentane unit.

The presence of long side substituents is a common property of the given group of natural antioxidants. The study of different forms of these substances has shown that they can react directly with hydrocarbon peroxy-radicals, i.e. they exhibit an antiradical activity.

Table 2. The rate constants for the interaction of peroxy-radicals with different forms of antioxidants.[6,94,98,103]

Antioxidant	k_7, litre mol^{-1} s^{-1}		
	quinone	hydroquinone	cyclic form
Tocopherols*			
α-Tocopherol	$(2.5\pm0.2)\cdot10^3$	$(4.7\pm0.5)\cdot10^6$	$(3.1\pm0.3)\cdot10^6$
β-Tocopherol	—	—	$(1.9\pm0.2)\cdot10^6$
γ-Tocopherol	—	—	$(1.4\pm0.1)\cdot10^6$
δ-Tocopherol	—	—	$(0.85\pm0.1)\cdot10^6$
Chroman-C11	—	—	$(3.2\pm0.3)\cdot10^6$
Chroman-C_6	—	—	$(2.9\pm0.1)\cdot10^6$
Chroman-C_1	—	—	$(3.2\pm0.3)\cdot10^6$
Ubiquinones**			
Ubiquinone Q-0	—	$(3.3\pm0.1)\cdot10^5$	—
Ubiquinone Q-2	—	$(3.1\pm0.1)\cdot10^5$	—
Ubiquinone Q-6	$(3.0\pm0.3)\cdot10^2$	$(3.1\pm0.2)\cdot10^5$	$(1.4\pm0.1)\cdot10^5$
Ubiquinone Q-9	$(2.8\pm0.2)\cdot10^2$	$(3.6\pm0.3)\cdot10^5$	—
Ubiquinone Q-10	—	$(3.3\pm0.1)\cdot10^5$	—
Vitamins K_1***			
Vitamin K_1 (20)******	$(2.1\pm0.2)\cdot10^2$	$(5.8\pm0.4)\cdot10^6$	—
Vitamin K_1 (15)	$(1.9\pm0.2)\cdot10^2$	—	—
Vitamin K_1 (5)	$(1.3\pm0.1)\cdot10^2$	—	—

*Measurement at 60 °C.
**Measurement at 50 °C.
***Measurement at 37 °C.
****The numeral in brackets indicates the number of carbon atoms in the side chain of the vitamin K_1 molecule.

Table 2 lists the constants for the reactions of natural antioxidants with peroxy-radicals. It is seen that only the reduced forms of the natural antioxidants, which have rate constants for their interaction with peroxy-radicals of the order of 10^5–10^6 litre mol^{-1} s^{-1}, exhibit an appreciable antiradical activity. The reduced form of vitamin K_1 has the highest constant $k_7 = (5.8 \pm 0.4) \times 10^6$ litre mol^{-1} s^{-1}. The antiradical activity of the phenolic forms of tocopherols

(homologues and analogues) is of the same order of magnitude (10^6 litre mol^{-1} s^{-1}). Ubiquinones and ubichromenols have constants k_7 amounting to 10^5 litre mol^{-1} s^{-1} and for the cyclic form, which has only one hydroxy-group, k_7 is smaller by a factor of 2 than for the hydroquinone form.[92-94]

For the quinone forms of tocopherols, ubiquinones, and vitamin K, the rate constants for this reaction are lower by two orders of magnitude. The esters (tocopheryl acetate) hardly react with free radicals.[92]

Thus the ability to inhibit the peroxide oxidation reaction of lipids is characteristic only of the reduced forms of natural antioxidants and is associated with the presence of the hydroxy-group in the molecule.

Since among all the reduced forms of the natural antioxidants tocopherols are the most stable, the antiradical activity of substances of different structures, differing in the number of substituents in the benzene ring of the chroman nucleus (homologues) and in the length of the aliphatic substituent in the 2-position (analogues), containing between 16 and 1 carbon atoms (chromans), has been investigated in relation to tocopherols. It has been established that the rate constants for the interaction of all the tocopherols investigated with peroxy-radicals are of the order of 10^6 litre mol^{-1} s^{-1} and the activation energies for this reaction are in the range 12.5–15 kJ mol^{-1}.[92]

The tocopherol homologues encountered in nature in different plants differ in the number and positions of the CH_3 groups in the benzene ring of the chroman nucleus but always have the same side substituents in the 2-position. It has been established[92] that the successive introduction of methyl groups in the 5-, 7-, and 8-positions in the tocopherol molecule increases the constant k_7. All these data agree well with experiments on the photolysis of tocopherols and with their oxidation-reduction potentials.[96,97]

Comparison of the antiradical activities of synthetic analogues of α-tocopherol, which are not encountered in nature, has shown[92,98] that the length of the phytyl side chains does not influence significantly such activity: the shortening of the side chain by each isopentane unit (5 carbon atoms) decreases the constant k_7 by 10–15% (Table 1). The introduction of one double bond into the side chain has approximately the same effect.

Analogous data have been obtained by Ingold and coworkers[99] for α-tocopherol and chroman C_1, which has a methyl group in the 2-position. The constants k_7 for the ubiquinones Q-2 and Q-10, differing by eight isopentane units, are hardly different (Table 2).[94] The values of k_7 for the synthetic analogues of vitamin K_1 change when the chain is shortened by two isopentane units by not more than 30% (Table 2). Consequently, the length and the degree of unsaturation of the side chain in the molecules of natural antioxidants do not exert an appreciable influence on the rate of their reaction with peroxy-radicals. Bearing this in mind, one may conclude, on the basis of a comparison of the constants k_7 for tocopherol and the cyclic form of ubiquinone (ubichromenol), that the replacement of the CH_3 group by the methoxy-group lowers the antiradical activity by a factor greater than 10.[93,94]

An analogous dependence has been observed also for the hydroquinone forms of vitamin K and the ubiquinol QH_2-6, whose constants differ by an order of magnitude.

Thus natural antioxidants have a labile hydroxy-group and react comparatively readily with hydrocarbon peroxy-radicals. The substituent in the *o*-position with respect to the hydroxy-group has a significant influence on the antiradical activity of natural antioxidants. Aliphatic side substituents have only a weak influence on the antiradical activity of such antioxidants.

Comparison of the overall antiradical activities of the natural antioxidants present in the lipids of the livers of intact animals and of individual antioxidants showed that they are comparable to the activities of the reduced form of vitamin K_1 and α-tocopherol.

However, the reduced form of vitamin K_1 is unstable and in the lipids which have been isolated vitamin K_1 can exist only in the form of a quinone and the activity of the total natural antioxidants can be usefully compared only with that of α-tocopherol. For lipids, this quantity proved to be 1.5 times lower than the activity of α-tocopherol, which we believe to be associated with the presence in lipids of antioxidants having a lower antiradical activity than that of tocopherol.

It is of interest to note that natural antioxidants have constants k_7 higher by 1–2 orders of magnitude than the majority of the phenols most widely used as antioxidants.[100] The activation energies for the interaction of peroxy-radicals derived from ethylbenzene with tocopherols of different structure (12–15 kJ mol^{-1})[92] and with ubiquinone QH_2-9 (17.4 ± 3.3 kJ mol^{-1} [94]) are lower than the corresponding value for the reaction with ionol (E = 20.5 kJ mol^{-1}).[101,102] On the basis of the low activation energies for the reactions involving the termination of peroxy-radicals by the molecules of natural antioxidants and the high rate constants for these reactions, it might have been expected that the above substances would inhibit the oxidation of model systems more effectively than synthetic phenols. However, in model low-temperature autoxidation systems (the most varied systems including both simple and complex systems) natural antioxidants proved to be much less active in inhibiting oxidation than synthetic antioxidants such as ionol, butoxyanisole, propyl gallate, and nordihydroguaiaretic acid, which has the constant $k_7 = 10^4$–10^5 litre mol^{-1} s^{-1}. Tests carried out by different investigators on tocopherols established that the efficiency of their antioxidant action varies in a complex manner with their concentration, the degree of unsaturation of the substrate, and the oxidation temperature.

Our analysis of the kinetic curves for the oxidation in the presence of tocopherols obtained in our own experiments and taken from the investigations of other workers,[92,103-106] showed that in all cases the dependence of the induction period of the oxidation reaction on the tocopherol concentration is unusual. Whereas for the majority of synthetic inhibitors the dependence of the efficiency of the inhibition on concentration is hyperbolic, for tocopherols the corresponding dependence passes through an extremum with the maximum inhibition effect at a specific concentration.[103] This maximum efficiency of the action of tocopherols is shown most markedly at low oxidation temperatures (at 20° and 40 °C). Comparison of the antioxidant activities of different tocopherol homologues showed that this type of relation with an extremum is characteristic of all the homologues, is independent of the oxidation substrate, and is most marked for α-tocopherol.[103] For the α-tocopherol analogues with short side substituents, the deviation from linearity and a decrease of the inhibiting effect with increase of their concentration have also been established,[92] i.e. the length of the side chain did not exert a significant influence on this feature of tocopherols. In all probability this unusual feature of the antioxidant activity of tocopherols is characteristic of the 6-hydroxychroman molecules themselves and is associated with the activity and stability of the radicals formed from them.

The elementary oxidation reactions involving the antioxidants and their radicals are examined in Scheme 2. The weakening of the antioxidant activity of tocopherols can be accounted for by the occurrence in the oxidation system of side reactions with participation of tocopherol or its radicals. Such reactions may be those of the inhibitor radical with a

hydrocarbon molecule [reaction (10)] and with a hydroperoxide molecule [reaction (7)] and the reaction of the inhibitor with the hydroperoxide [reaction (11)] or with oxygen [reaction (12)]. The rates of these reactions depend significantly on the structure of the antioxidant and the oxidation condition. We were interested in the properties of tocopherols under conditions close to physiological conditions: a low oxidation temperature (20–40 °C), a low degree of oxidation, and a high degree of unsaturation of the substrate.

Scheme 2

$$InH + RO_2^{\cdot} \underset{k_{-7}}{\overset{k_7}{\rightleftarrows}} ROOH + In^{\cdot} \qquad (7), (-7)$$

$$\left.\begin{array}{l} RO_2^{\cdot} + In^{\cdot} \xrightarrow{k_8} \text{molecular products} \\ In^{\cdot} + In^{\cdot} \xrightarrow{k_9} \text{molecular products} \end{array}\right\} \text{chain termination;} \qquad \begin{array}{l}(8)\\(9)\end{array}$$

$$In^{\cdot} + RH \xrightarrow[+O_2]{k_{10}} RO_2^{\cdot} + \text{molecular products} \quad \text{chain propagation,} \qquad (10)$$

$$InH + ROOH \xrightarrow{k_{11}} \text{molecular products} + \text{free radicals;} \qquad (11)$$

$$InH + O_2 \xrightarrow{k_{12}} In^{\cdot} + HO_2^{\cdot} \qquad (12)$$

HIn = inhibitor.

Under these conditions, the oxidation reaction of tocopherol itself [reaction (12)] may be neglected, since tocopherols are stable even on heating to 100 °C.[107]

Under the conditions of a low degree of oxidation, where the concentration of hydroperoxides in the substrate is low, it is possible to neglect reactions (−7) and (11). It remains to consider the possibility of the occurrence of reaction (10).

Reaction (10) was introduced into the scheme for the inhibited oxidation of hydrocarbons in order to calculate the rate constants from chemiluminescence data.[95,108] Depending on the constants k_6, k_8, and k_9, whose ratios make it possible to estimate the limits within which the constant k_{10} varies for α-tocopherol in the initiated ethylbenzene oxidation model, k_{10} is in the range $(0.5–1.2) \times 10^{-1}$ litre mol^{-1} s^{-1}, i.e. cannot be neglected in estimating the antioxidant activity.[92]

The ratio of the rates of the reactions which decrease the efficiency of the action of antioxidants can vary with the concentration of free radicals, since an increase of the rate of initiation W_i entails a quadratic increase of the rates of reactions (8) and (9) and a linear increase of the rate of reaction (10). Thus, with increase of W_i in the system, the contribution of the chain propagation by the antioxidant radical to the overall rate of oxidation diminishes, i.e. the efficiency of the antioxidant increases. An extended kinetic scheme for the oxidation of hydrocarbons has been examined[95] and relations confirming the increase of the efficiency of the antioxidants with increasing concentration of free radicals in the system have been obtained. This explains the finding that natural antioxidants exhibit the greatest efficiency in models involving the oxidation of highly unsaturated aliphatic acids.

If this oxidation system contains substances capable of removing from the reaction sphere the radicals of natural antioxidants or substances which regenerate their oxidised forms, a synergistic effect should be observed under these conditions. The role of synergists is usually assumed by substances having a low-oxidation-reduction potential and which readily pass from the oxidised to the reduced form (for example, ascorbic and citric acids).[45,109] For tocopherols, synergism with dibasic organic acids was established as early as 1942.[111]

It has been shown recently by direct experiments[112] that ascorbic acid reacts directly with tocopherol radicals, which is accompanied by an increase of the concentration of ascorbic acid radicals, while that of the tocopherol radicals falls.

We shall consider which properties of membrane lipids and natural antioxidants ensure a high efficiency of the regulation of the peroxide oxidation of lipids. As already stated, the oxidative processes occurring in membranes have their characteristic features: a structured lipid double layer, the multicomponent composition of the lipids, a high degree of unsaturation of the aliphatic acids forming part of the composition of the membrane phospholipids, and the presence in the latter of substances capable of intensifying or weakening the action of natural antioxidants.

It has been shown in a recently published study[113] that the activity of tocopherols in structured substrates is higher by 1–2 orders of magnitude compared with oxidation in the liquid phase. The authors believe that such increase of activity is associated with the fact that the OH groups of the tocopherols in the structured substrate are directed towards the hydrophilic medium. If radical species of the type of OH^- and O_2^- approach the membrane from this medium, then their termination by the tocopherol molecules is more effective the greater the number of hydroxy-groups of the antioxidants are present on the outer surface of the membrane.

The maximum inhibition of the oxidation reaction by natural antioxidants in model systems can be achieved in the oxidation of highly unsaturated substrates with a low content of peroxides and at low temperatures. Such conditions are in fact characteristic of the oxidation of lipids in biomembranes, i.e. the physiological conditions are optimal for the manifestation of the antioxidant activity of natural antioxidants. The high antiradical activities of natural antioxidants constitute the basis of the sharp change in the rate of the peroxide oxidation of lipids, which ensures a high effectiveness of regulation even when their concentration is altered only slightly.[106]

Since the reduced phenolic forms of natural antioxidants have constants k_7 higher by a factor of 100–1000 than those for quinones, the transition of natural antioxidants from one form to another, involving an appreciable decrease or increase of the antiradical activity, can also be regarded as a means for a rapid change in the intensity of the oxidative reactions occurring in lipids.[106,114]

The question arises whether ubiquinones and vitamins K_1, having unstable reduced forms which are readily converted into inactive quinones, can be regarded as natural antioxidants. In all probability they can be so regarded, because lipids always contain different reducing agents and enzymes capable of converting the quinones into the phenolic form.

Furthermore, one should bear in mind that in a lipid environment the stability of the phenolic forms of these compounds is higher. The question also arises whether the radicals formed from the antioxidant molecules can be active within the membrane. It has been established in experiments on animals that the relation between the antioxidant activity of lipids and the amount of natural antioxidants present in them passes through an extremum, as in model systems.[92] This permits the conclusion that the properties of weak antioxidants, established for them in model experiments, are characteristic of the natural antioxidants also in systems *in vivo*. This feature of the antioxidant activity of natural antioxidants can also be regarded as regulatory; in the presence of an excess of such substances in lipids, their inhibiting activity falls. We believe that the radicals formed from natural antioxidants fulfill, as it were, the role of a buffer which maintains the rate of oxidation of lipids at a specific level.[43,114]

Phenomena of this kind, namely a sharp change in efficiency following a slight increase in the concentration of the given substance up to the reversal of the effect, were first discovered and investigated in detail by Academician N.M.Emanuel' and were called the "critical phenomena" in inhibited liquid-phase oxidation reactions.[44]

In model hydrocarbon oxidation reactions, it was found that variable-valence metal ions at low concentrations activate the oxidation reaction, catalysing the decomposition of hydroperoxides, while at high concentrations they inhibit such reactions. The same type of relation has been established for Fe^{2+} ions in a study of the oxidation of lipids in membranes.[69] Retinol activates the oxidation of liposomes when present in small doses and stabilises them when present in large doses.[9,68] Such dual activity apparently constitutes a means for a rapid alteration of the rate of oxidation (regulation by the concentration).

A change in the composition of the membrane lipids, leading to a change in the rate of peroxide oxidation by altering the rate of initiation, has a significant influence on the rate of the reactions involving chain propagation by the radicals formed from natural antioxidants [reaction (10)]. Thus it has been established[95] that the contribution of the rate of reaction (10) to the antioxidant activity of natural antioxidants is less significant for higher rates of initiation and for a high degree of unsaturation of the oxidation substrate (regulation by the substrate).

Natural antioxidants participate in the regulation of the peroxide oxidation of lipids not as independent substances but as interacting components of a single system. The possibility of changing the concentration and activity of one set of natural antioxidants by administering others to animals constitutes proof of the validity of this postulate. For example, after a single administration of α-tocopheryl acetate (200 mg kg^{-1}) to intact animals, an increase of the concentration of the total antioxidants is observed in the liver lipids (by a factor of 37), while the amount of free α-tocopherol increases by a factor of only 10 during the same period.[5] An increase of the amount of a particular natural antioxidant is possible only when the product of the antiradical activity of the administered antioxidant and its concentration (k_7c) is comparable to the same product for the antioxidants present in the cell.[5]

At the same time one should bear in mind that the transformation of the relatively inactive forms of antioxidants into highly reactive forms is possible in the cell, so that, after the introduction of, for example, quinones, which can be reduced to phenols, an increase of the total amount of natural antioxidants is also observed.[115] Although ubiquinone and vitamin K_1 in the form of quinones cannot compete with tocopherols, in the reduced forms, as hydroquinones or ubichromenol, they can replace tocopherol in free-radical oxidation reactions.

After the introduction of vitamin K_1, not only an increase of the amount of natural antioxidants in lipids but also an increase of the activity of the lipids of the experimental animals compared with that of the control lipids was established, i.e. substances whose antiradical activity is greater than the total activity of the natural antioxidants and even greater than the activity of pure α-tocopherol accumulate in the lipids. Only the reduced form of vitamin K_1 exhibits such a high activity.[6]

The data presented confirm our hypothesis that tocopherols, ubiquinones, and vitamins of the K group are interrelated in the organism via their antioxidant functions. The question whether the system of natural antioxidants is linked with other systems regulating the peroxide oxidation of lipids remains open. In the first place one should note that it is difficult to draw a clear-cut boundary between these systems. Indeed, the phenolic forms of natural antioxidants are typical antioxidants, but at the same time they play the role of structural factors and on this basis can be assigned to the protective system I. On the other hand, quinones, which are potential antioxidants, can interact with $O_2^{\cdot-}$ (system II) to form semi-quinone radicals.[46,116,117] This results not only in the destruction of the possible oxidation initiation centres ($O_2^{\cdot-}$) but also in the formation of semiquinone radicals capable of terminating the oxidation chain on recombination with the lipid peroxy-radicals or on interaction with the OH group of the semiquinone. This leads to the simultaneous destruction of the oxidation initiation centres and the appearance of active free radical acceptors, which makes it possible to regard this reaction as a means for the inclusion of the oxidised forms of antioxidants in the regulation of the intensity of the peroxide oxidation of lipids in response to the increase of the rate of initiation of the oxidation process.

In all the cases considered, the interrelation of different systems for the regulation of the peroxide oxidation of lipids is based on physicochemical characteristics.

However, one must not forget also the biochemical mechanisms of such inter-actions. Thus it has been shown[24,26,35] that there exists a system for the maintenance of the steady-state in the peroxide oxidation of lipids, based on the relation between the rate of the peroxide oxidation of lipids and the rate of change of their composition. In response to the intensification of the peroxide oxidation of lipids, the composition of the lipids changes in such a way that they become more resistant to oxidation.[24] The presence of such a relation complicates the consideration of the characteristic features of the regulation of the peroxide oxidation of lipids but it enables the cell to switch the rate of the peroxide oxidation and the associated metabolism to a new level in response to the action of endogenic and exogenic factors. This has the consequence of a change in the structure and ultimately in the functional activity of the membrane.

The steady state nature of the lipid oxidation process constitutes the basis for the maintenance of a specific composition, structure, and function of membranes as highly specific, complex, and multicomponent systems. The membrane lipids fulfill a dual function: on the one hand, they maintain a rigorously specified structural organisation of the membranes, responsible for the effective fulfillment of their biological functions, and, on the other hand, they ensure the lability of their composition and the rapid response of the cell to changes in the organism.

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Kinetics of the Radiation-induced and Photochemical Oxidation of Biomacromolecules in Aqueous Solutions

I.I.Sapezhinskii

The sequence of radiation-induced photochemical reactions of proteins, nucleic acids, and other biological species has been investigated: the primary stages in the formation of free macroradicals and other active products and their reactions leading to the modification of the primary structure of the biopolymers. Simplified versions of kinetic schemes which describe satisfactorily the experimental data are discussed. The redistribution of the initial damage-induced defects in protein-DNA-other cell components systems has been subjected to a formal kinetic analysis.
The bibliography includes 129 references.

CONTENTS

I. Introduction 918
II. The yields of radiation-induced and photochemical reactions of proteins and nucleic acids 919
III. The rate constants for the possible free-radical reactions involving biopolymers 920
IV. Kinetics of the reactions of free macroradicals in solution 921
V. The primary processes in the radiation-induced oxidation 923
VI. Kinetic scheme for sensitised photochemical oxidation 924
VII. Photophysical and photochemical reactions occurring when macromolecules are acted upon by ultraviolet radiation 925
VIII. The possible redistribution processes involving the initial damage-induced defects in multicomponent systems containing DNA, proteins, and other substances 926

I. INTRODUCTION

The question of the primary mechanisms of the action of light and ionising radiation on the principal biochemical components of the cell is one of the essential questions in radiobiology and destructive photobiology. As early as the middle 1950's, Academician N.M.Emanuel', who was engaged in the study of the kinetics of liquid-phase oxidation reactions, put forward a broad programme for the study of radiation-induced and photochemical reactions of proteins, nucleic acids, and lipids. Extremely simplified and fairly naive ideas about these processes were current at that time. This programme involved the study of the degradation of biomacromolecules by methods which were new at the time: EPR, pulse radiolysis, and flash photolysis. This review includes certain results obtained in the course of the execution of this programme.

The sequence of the effects of optical and ionising radiation on living organisms can be subdivided very arbitrarily and with much simplification into three stages. The first stage includes the entire set of the physicochemical primary processes from the instant of irradiation up to the formation of relatively stable products of the radiation-induced and photochemical modifications of the primary structure of the biopolymer. The second stage is molecular-biological and in it numerous enzymes systems for the repair of DNA molecules begin to operate, which leads to both the elimination of the modified sections of the nucleic acids and to the appearance of additional DNA structural defects. Finally, the third stage includes further processes which entail damage of the genetic material in the cells, organs, and tissues and this leads to the distortion of metabolism, the breakdown of the regulatory systems, and finally to biological effects. This review has a bearing only on the first, physicochemical stage—the action of radiation on proteins, DNA, and other components of the cell.

Proteins perform catalytic, transport, protective, immune, supporting and other functions in the living cell, forming part of the composition of all the cell organelles and their content amounts of 50% and above of the dry weight of living organisms. This is why, on exposure to light and ionising radiation, proteins bear the brunt of the radiation-induced stress and constitute in this sense the principal "chemical target" of the action of radiation. At the same time DNA macromolecules are the main "biological target", because damage to such molecules entails in most cases biological effects.

Radiation-induced and photochemical reactions of macromolecules involve numerous and varied reactions of free radicals, electronically excited states of the macromolecules, peroxy-radicals, peroxides, and other active species. Protein molecules are the most complex macromolecules with numerous groups which are modified by radiation. The discovery of all such changes is a task for the future and this applies, albeit to a lesser extent, to DNA.

During the last 20 years, there has been a qualitative leap forward in the understanding of the mechanisms of the radiation-induced and photochemical degradation of biopolymers. The use of EPR, pulse radiolysis, and flash photolysis makes it possible to discover tens of different intermediates participating in the degradation of proteins and nucleic acids: these are the active products of the radiolysis of water, numerous types of free macromolecules and peroxy-radicals, electronically excited states of aromatic groups of proteins and DNA bases, the radical-ions derived from the macromolecules, photoinitiators and radiosensitisers, singlet oxygen, and various peroxides. Naturally, the contribution of a particular species to the overall degradation process is determined by its yield and the kinetic characteristics of the possible competing reactions. The first aim of the present review was therefore a kinetic examination of the most probable processes and the simplest of the possible kinetic schemes which describe satisfactorily the experimental data.

In the living cell proteins compete with other molecules, including DNA, for the active species produced by photolysis and radiolysis and the second aim of the review was therefore a formal-kinetic examination of the redistribution of the initial damage-induced defects in multicomponent systems at concentrations comparable to those within the cell.

The inclusion in a single article of results concerning different influences on the macromolecules by ionising radiation, ultraviolet (u.v.) light, as well as light in the presence of photosensitisers is not surprising because many products of these reactions are the same and the kinetics of their behaviour are also similar. An exception is apparently the effect of u.v. light on DNA, in which the main photoproducts (pyrimidine dimers) are formed directly from the singlet and triplet electronically excited state without the participation of other intermediates.

II. THE YIELDS OF RADIATION-INDUCED AND PHOTOCHEMICAL REACTIONS OF PROTEINS AND NUCLEIC ACIDS

The study of radiation-induced or photochemical reactions of biomacromolecules has a history of almost 100 years. The total number of studies exceeded 10 000 long ago. Conferences are being held regularly and reviews devoted to the primary photochemical and radiation-induced reactions of proteins and DNA both in solutions and at the level of living cells are being published.[1-34]

Among the many thousands of applications, only a few contain quantitative data suitable for the construction of the possible reaction mechanisms—these are data concerning the yields of the modified groups, the disappearance of the initial groups, and the dependence of the observed effects on a broad spectrum of experimental conditions: the irradiation dose rate, the concentrations of the macromolecules, oxygen, and various additives, and temperature. Very few studies have been devoted specifically to the radiation-induced and photochemical oxidation of macromolecules, which is apparently associated with the rapidly increasing set of intermediates and final oxidation products. The lack of interest in the photochemical oxidation of biopolymers has been promoted also by the fact that certain photobiological effects of u.v. light are independent on the oxygen concentration, although photochemical oxidation reactions do naturally occur under these conditions.

Table 1. The radiation-chemical yields in the absorption of oxygen by solutions of nucleic acids (molecules/100 eV) at different temperatures and irradiation dose rates.[36]

Substance	c, M	0.4 Gr s^{-1}; 20 °C	0.04 Gr s^{-1}		
			5° C	20° C	50° C
Single-stranded DNA	$7\cdot10^{-4}$	6.8	—	6.6	—
	$4\cdot10^{-3}$	7.5	8.3	8.6	9.2
Double-stranded DNA	$7\cdot10^{-4}$	4.6	—	4.4	—
	$4\cdot10^{-3}$	—	4.7	—	—
RNA	$7\cdot10^{-4}$	4.0	5.0	5.4	6.6
Poly(U)	$2\cdot10^{-4}$	14.6*	17	—	—
	10^{-3}	21	—	—	—

*At 5 °C.

The principal overall characteristic of the oxidation processes is the rate of absorption of oxygen on irradiation—the radiation-chemical or quantum yield in the consumption of oxygen. Unfortunately there are few quantitative data for these quantities, although the methods for the determination of the rate of oxidation are extremely simple and the first studies on the absorption of oxygen using the Warburg apparatus were published about 60 years ago.[35]

Table 1 presents the radiation-chemical yields in the absorption of oxygen by solutions of natural nucleic acids and synthetic polyuridylic acid [poly(U)].[36] Evidently the yields for single-stranded DNA vary from 6.8 to 9.2 O_2 molecules per 100 eV depending on the experimental conditions. For double-stranded DNA, the yields are somewhat smaller (4.4–4.7). The yields in the case of RNA are 4–6.6 O_2 molecules per 100 eV. The maximum yields have been obtained for poly(U) (up to 21). Some increase of the yield with decrease of the dose rate and with increase of the temperature of single-stranded DNA, RNA, and poly(U) is striking. These results have been explained[36] by the occurrence of chain reactions with short chains and a scheme has been published for the reactions of free radicals derived from nucleic acids, the confirmation of which requires additional data. The radiation-chemical yields for the absorption of oxygen by proteins are in the range 2–4 O_2 molecules per 100 eV.[37]

Table 2 presents the possible participants in the radiation-induced and photochemical reactions of proteins (B) and nucleic acids (D). The yield in the absorption of oxygen in the radiation-induced oxidation of proteins and nucleic acids are comparable. The quantum yields of the sensitised and unsensitised photochemical oxidation of proteins are fairly high owing to the presence in the proteins of the readily oxidisable tryptophan, tyrosine, cysteine, cystine, methionine, and histidine residues. The quantum yields in the photochemical oxidation of DNA are extremely low. If it is assumed that the breaks in DNA arise in reactions involving free radicals, then the yield of the photochemical oxidation of DNA is of the order of 10^{-4}% according to Zavilgelsky et al.[32]

The active products of the radiolysis of water (Table 2, Nos. 3–7) are obligatory participants of the radiation-induced oxidation reactions. The contribution of each can be discovered with the aid of relatively selective acceptors. For hydrated electrons, this is nitric oxide, while for hydroxy-radicals the acceptors are alcohols and sugars. The superoxide radical-ion (O_2^-) or the hydroperoxy-radical are apparently involved in all types of oxidation of macromolecules. Singlet oxygen is almost always formed in sensitised photochemical oxidation, but its formation under influences of other types is problematical.[36]

Other inorganic and organic radicals may be formed in the photolysis and radiolysis of the additives introduced and they can interact fairly effectively with macromolecules. Low-molecular-weight peroxy-radicals react effectively with proteins and less so with DNA.[39-51]

Photosensitisers in singlet and triplet electronically excited states participate in the sensitised photochemical oxidation of biopolymers and the reaction mechanisms can be extremely varied.[38]

The free radicals derived from proteins and nucleic acids are formed under all types of influences. It is noteworthy that the very concept of "free macro-radicals" is fairly arbitrary, because irradiation results in the formation of a large set of radical species of different types. For proteins, these are the radical-anion and the free radical obtained from the peptide unit and the lysine, arginine, phenylalanine, tyrosine, cysteine, cystine, methionine, aspartic acid, glutamic acid, and proline free radicals.[52-60] Other types of radicals have also been suggested. For DNA, these are the thymine free radical and radical-anion, the guanine radical-cations, and free peroxy-radicals.[61-64] The study of the reactions of single-stranded DNA by pulse radiolysis led to the detection of cytosine, guanine, and adenine radicals.[65] Apparently the overall yield of protein and DNA free radicals, when these are present at high concentrations, can reach six radicals/100 eV under the conditions of complete trapping of the water radiolysis product. The quantum yields in the

formation of radicals when DNA and proteins are acted upon by ultraviolet light have not yet been measured; at a low temperature radicals are formed as a result of two-quantum reactions[66,67] and the concept of quantum yield is extremely relative. Protein and DNA peroxy-radicals are formed under all types of influences, but their yields are unknown. The electronically excited states of the protein and DNA groups naturally arise on exposure to u.v. light and the yields of the triplet states apparently reach several per cent. On sensitisation, there is a possibility of the population of the triplet levels by energy transfer from suitable sensitiser levels. In radiolysis the yields of the excited states in solutions of biopolymers are low[68] and it has been suggested that they are formed as a result of the Vavilov–Cherenkov radiation.[69–71]

Table 2. The radiation-chemical (molecules/100 eV) and quantum (%) yields in the oxidation or formation of particular products of the reactions of proteins (B) or DNA (D).[1–71]

No.	Initial, intermediate, or final products of the reactions of proteins and DNA	RIR	PSR	PCR
1	$O_2 + B \rightarrow \dot{R}_B$	2—4	1—10	0.2—2
2	$O_2 + D \rightarrow R_D$	4—8	+	+
3	$\dot{O}H$	2.7	—	—
4	$\dot{e}$	2.7	+—	+
5	$\dot{H}$	0.6	+—	+—
6	H_2O_2	0.9	+—	+—
7	O_2^-, $H\dot{O}_2$	+	+	+
8	$^1O_2$	?	0—100	?
9	$\dot{R}_{inorg}$	+	+	+
10	$\dot{R}_{org}$	+	+	+
11	$R\dot{O}_2$	+	+	+
12	^1S	—	+	—
13	^3S	—	+	—
14	$\dot{R}_B$	3	+	+
15	$\dot{R}_D$	3	+	+
16	$R\dot{O}_{2B}$	+	+	+
17	$R\dot{O}_{2D}$	+	+	+
18	^1B	?	—	+
19	^3B	?	+—	+
20	^1D	?	+—	+—
21	^3D	?	+	+
22	Π	1	+	+
23	Single breaks in DNA	0.5—1	+	+
24	Double breaks in DNA	0.01	+	+
25	Breaks in the peptide bonds in proteins	+	+	+
26	Decomposition of DNA bases	1—2	+	+
27	Decomposition of aminoacid residues of protein	2	1—3%	1%
28	Cyclobutane dimers in DNA	?	+	1—4%
29	Cross-links	+	+	+
30	DNA–protein cross-links	+	+	+
31	Inactivation of DNA	+	+	+
32	Inactivation of enzymes	0.01—3	0.1—10%	0.1—10%

Notation: RIR = radiation-induced reactions, PSR = photosensitised reactions, and PCR = photochemical reactions of protein and DNA macromolecules; the "+" sign refers to reactions with species whose participation in the processes has been reliably established, the "+-" sign refers to their possible participation, the "-" sign shows that they are not involved, and the "?" indicates their tentative involvement; $\dot{R}_{inorg}$ and $\dot{R}_{org}$ are the free radicals arising in photolysis or in radiolysis in the presence of inorganic or organic additives, ^1S and ^3S are the singlet and triplet electronically excited states of the photosensitisers, $^1O_2$ is singlet oxygen, $\dot{R}_B$ are protein free radicals of various types, $\dot{R}_D$ are DNA radicals, $R\dot{O}_{2B}$ and $R\dot{O}_{2D}$ are protein and DNA peroxy-radicals, ^1B and ^3B are the singlet and triplet electronically excited states of the aromatic groups of the protein, ^1D and ^3D are the corresponding states of the DNA bases, and π are stable and unstable peroxides derived from the macromolecules.

Unstable and stable peroxides (Table 2, No.22) are formed under all types of influences on the macromolecules in the presence of oxygen; the radiation-chemical yield in their formation, amounting to about one molecule/100 eV, is apparently significantly too low because of the occurrence of subsequent rapid reactions.

Table 2 (Nos.23–30) presents certain recorded changes in the macromolecule on exposure to light and ionising radiation. They are numerous and apart from these there are apparently also others hitherto undiscovered because the overall yield in the absorption of oxygen is greater than the sum of the yields of the known damage-induced defects.

Single and double breaks on γ-irradiation, the formation of cyclobutane dimers on u.v. irradiation, and the formation of "protein–DNA" cross-links under all types of influences can be included in the biologically significant damage to DNA. It is believed that the last type of damage is least well repaired by the numerous enzyme cell repair systems.

Table 2 shows that there are numerous data concerning the radiation-induced oxidation and other reactions of proteins and DNA. It is also seen that in many cases there are no quantitative data. This so far precludes the determination of a relatively complete picture of the reactions.

III. THE RATE CONSTANTS FOR THE POSSIBLE FREE-RADICAL REACTIONS INVOLVING BIOPOLYMERS

The rate constants for the free-radical reactions are obtained by pulse methods or are calculated from the dependence of the rate of the process on the concentration of the substrate, oxygen, or various added acceptors. It is noteworthy that the very concept of the rate constants for reactions involving protein and DNA macromolecules is fairly arbitrary. The effective rate constant for the reaction of a macromolecule with any species includes the sum of the partial rate constants for the reactions through individual groups of the polymer with these species. For DNA molecutes the rate constants were calculated either in relation to the concentration of the monomeric units or in relation to some fragment of the macromolecule or the entire polymer molecule—all these possibilities are used in the literature and the data must be recalculated.

The presence of large errors in the constants calculated using fairly complex kinetic schemes and with incomplete allowance for competing reactions is significant. In the general case many rate constants are correct within the limits of an order of magnitude. The Tables below present the averaged rate constants for proteins, DNA, lipids, and other substances, taken and recalculated from reviews quoted in previous Sections. Preference has been given to data obtained from the concentration variations. In the case of proteins data are quoted for the "average" protein with a molecular weight of $(2–4) \times 10^4$ and for DNA data are presented for molecules with a molecular weight of 4×10^4. It is noteworthy that the rate constants are similar to the diffusion constants and vary little with molecular weight. The situation is more complex for lipid membranes which can incorporate hundreds of a wide variety of chemical compounds; phosphoglycerides, glycolipids, and cholesterol. Data referring to the most reactive unsaturated lipids are quoted for such membranes.

Table 3 presents estimates of the rate constants for bimolecular reactions of the active water radiolysis products and singlet oxygen with proteins, DNA, lipids, cysteamine (one of the best known radioprotectors), phenolic inhibitors of free-radical processes, typical nitro-compounds (radiosensitisers), and oxygen. The constants have been adjusted

to 25 °C. Evidently the hydrated electron and the hydroxy-radical interact effectively with all the substances enumerated above and the rate constants are highest for proteins and lowest for lipids. The radical-anion O_2^- is significantly less reactive, reacting sluggishly with proteins containing no metal atoms; in the use of the iron- and copper-containing proteins the rate constants reach 10^7 litre mol^{-1} s^{-1}. Cystamine, phenols, and nitro-compounds react effectively with superoxide. Singlet oxygen reacts fastest with proteins and phenols, while its reactions with DNA and lipids are relatively ineffective.

Table 3. The estimated rate constants for the reaction of active radiolysis and photolysis products with proteins, DNA, lipids, cysteamine, phenolic inhibitors of free radical processes, nitro-compound radiosensitisers, and oxygen (litre mol^{-1} s^{-1}). [11,12,25,26,31,32,37]

Substance	e^-	OH	O_2^-	$^1O_2$
Proteins	$5\cdot10^{10}$	$(1—6)\cdot10^{10}$	$<10^3$	$10^8—10^{10}$
DNA	$2\cdot10^{10}$	$(1—6)\cdot10^{10}$	$<10^3$	$<10^4$
Lipids	10^6	10^7	$<10^3$	$10^3—10^5$
Cysteamine	$2\cdot10^{10}$	$2\cdot10^{10}$	10^6	—
Phenols	10^9	10^{10}	$10^6—10^7$	$10^5—10^7$
Nitro-compounds	$2\cdot10^{10}$	10^9	$10^7—10^9$	—
Oxygen	$2\cdot10^{10}$	$4\cdot10^{9}$*	—	—

*At pH 11.

Table 4. The estimated rate constants for reactions of various free radicals and peroxides with certain substances (litre mol^{-1} s^{-1}). [11,14,22,25,37,38]

Substance	$\dot{R}_B$	$\dot{R}_D$	$\dot{R}$	$R\dot{O}_2$	$\dot{R}_H$	Π_1	Π_2
Proteins	$10^6—10^8$	$10^6—10^8$	$10^8—10^{10}$	$10^{-1}—10^3$	10^9	$10^{-3}—10^{-2}$	—
DNA	$10^3—10^4$	$10^3—10^4$	$10^3—10^4$	$10^{-2}—10^1$	10^{10}	—	—
Lipids	$<10^3$	$<10^3$	$10^6—10^7$	$10^{-2}—10^1$	—	—	—
Protectors	$10^7—10^8$	$10^7—10^8$	$10^7—10^8$	—	—	1—10	—
Phenols	$10^4—10^6$	$10^4—10^6$	$10^5—10^7$	$10^4—10^6$	—	0.1—5	—
Nitro-compounds	10^9	10^{10}	$10^7—10^8$	—	—	—	—
Oxygen	$10^8—10^9$	$10^8—10^9$	$10^6—10^9$	—	—	—	—
k	$10^1—10^4$	$10^3—10^6$	$10^6—10^8$	$10^4—10^8$	$10^6—10^8$	$10^{-1}—10^{-5}$	$10^{-1}—10^{-5}$

Notation: $\dot{R}$ are low-molecular-weight organic radicals, $R\dot{O}_2$ are peroxy-radicals, $\dot{R}_H$ are sensitiser free radicals, Π_1 are protein peroxodes, Π_2 are DNA peroxides, k are the rate constants for the destruction of the corresponding radicals in first- or second-order reactions (s^{-1}).

In a complex multicomponent system the primary damage induced both by water radiolysis products and by the direct action of radiation quanta and charged particles leads to secondary reactions, both intramolecular and intermolecular. Numerous reactions of free radicals and a redistribution of the initial defects among different components take place. In order to represent the entire picture of the redistribution of damage-induced defects, it is necessary to have data for the interaction of the majority of different types of free radicals with one another and also for their reactions with cell components.

Table 4 presents the rate constants for the reactions of protein, DNA, and lipid free radicals, peroxy-radicals, and protein and DNA peroxides with various substances. The estimated rate constants, obtained as a rule by competitive methods, are presented. The wide range of these values is due to the different chemical natures of the radicals. Proteins, cysteamine, inhibitors, aromatic nitro-compounds, and oxygen exhibit a high reactivity in relation to all the active species. The interaction of lipids and DNA with various radicals is characterised by lower rate constants. It is also seen that there are virtually no data for the reactions of protein and DNA peroxides. The rate constants will be used below in Section VIII in the examination of the formal kinetics of the distribution of damaged-induced defects in "protein–DNA" and "protein–lipids" systems.

IV. KINETICS OF THE REACTIONS OF FREE MACRORADICALS IN SOLUTION

There exists an extensive literature on the reactions and transformations of free radicals analogous to those formed in proteins and nucleic acids. [55,60,63,67] These are primarily reactions involving the abstraction of a hydrogen atom, which may result in the migration of the free valence "within" the protein globule or the double helix of DNA. Reactions of this type probably lead to the protection of macromolecules by protectors of the type of cysteine and cysteamine. Free radicals can subsequently add to molecules with double bonds and to aromatic groups. In addition the free radicals can undergo decomposition, isomerisation, recombination, and disproportionation reactions. Finally one may also mention oxidation-reduction reactions, for example, with variable-valence metal ions.

Protein and nucleic acid macromolecules can be regarded as miniature chemical reactors with a complex geometry and internal dynamics, in which rapid free radical processes take place. The rates of these reactions are limited, on the one hand, by the reactivity of particular radicals in relation to groups in close proximity and, on the other hand, by the rapid and slow movements "within" the macromolecules.

The main bulk of data for the reactions and transformations of protein and nucleic acid free radicals have been obtained in experiments by the EPR method on dry specimens and frozen solutions at low temperatures. The kinetic characteristics of the behaviour of radicals in solutions cannot be estimated from data for the radiolysis and photolysis in the solid phase. This is because of the unusual nature of the processes involving the accumulation and destruction of macroradicals in solid specimens for which the kinetic curves cannot be described within the framework of the usual ideas concerning reactions in the liquid and gaseous phases and it is necessary to introduce the concept of the polychromaticity of the rate constants, the rate constant distribution functions, and activation energies; a non-uniform distribution of radicals and the occurrence of reactions at the temperatures of the structural transitions in the matrices are characteristic of the solid phase. [55,60,63,67,72–76]

Certain data for the kinetics of the accumulation and destruction of protein free radicals have been obtained for aqueous protein solutions by EPR, pulse radiolysis, and flash photolysis. The main difficulty in comparing data obtained by different methods consists in the fact that apparently all the radicals except those which give rise to broad lines are recorded by EPR, while flash photolysis and pulse radiolysis record only the radicals which give rise to absorption bands

outside the region of absorption by the macromolecules, i.e. above 300 nm. In the main these are the cystinyl and tryptophanyl free radicals.

Kinetic curves have been obtained[77-80] for the accumulation and destruction of protein free radicals on u.v. irradiation of their solutions. It was found that there are two stages in the destruction of free radicals: one rapid stage with times of the order of 10^{-2}–10^{-1} s and another, slow stage with times in the range 1–20 s. The disappearance of free radicals formally follows a kinetic first-order reaction equation and bimolecular components have not been found. It has been shown for serum albumin that the rate constant for the slow stage depends only slightly on temperature when the latter is varied from 10° to 40 °C. The characteristics of the destruction of free radicals do not differ greatly for different proteins. It has been found that the contribution of the slow component is proportional to the content of the alpha-helix in the proteins, which made it possible to employ this correlation for the determination of the content of the helix in a series of protein-containing species.[80] It also follows from the data quoted above[77-80] that the rate of accumulation of free radicals is higher than the rate of their destruction; the slow component is hardly manifested. This constitutes direct indication that the radicals are effectively destroyed by the radiation.

The kinetics of the destruction of free radicals in solutions of egg albumin have been studied by pulse radiolysis.[81] The kinetic curves for the destruction of the free radicals can be described by a set of exponential components with effective rate constants of 440, 8 and 0.4 s^{-1} when the experiments were carried out with the solution saturated by N_2O (the hydroxy-radicals react) and with approximately the same values on irradiation in an atmosphere of nitrogen. Analogous results have been obtained also for other proteins.[82-91]

The time scale of the reactions of the DNA free radicals in solutions at room temperature is extremely wide, ranging from microseconds to seconds.[65,92] A study[92] demonstrating the liberation of the K^+ and H^+ ions on irradiation of the potassium salt of polyuridylic acid in solution is of interest. This effect is treated as one involving the rupture of the poly(U) chain, entailing an increase in the degree of dissociation. It has been shown by pulse radiolysis with conductimetric measurements that the kinetics of the liberation of the ions are described by an equation for a first-order reaction with a rate constant of 0.8 s^{-1}. It has been suggested that the breaks in poly(U) are produced as a result of the decomposition of the poly(U) radicals formed when the polymer is attacked by hydroxy-radicals. The destruction of the macroradicals in first- and not second-order reactions is not very surprising, since analogous effects have been observed also in other systems. The free valence probably "moves" along the macromolecule, leaving behind a trail of transformations and the duration of this movement is rate-limiting. Next there are two possibilities: either there is a reaction between two macroradicals or a low-molecular-weight radical is initially split off from the macroradical and reacts with a polymeric radical. It is easy to show that the required disproportionation rate constant should not be less than 10^7–10^{10} litre $mole^{-1}$ s^{-1} and only then is it possible to account for the exponential character of the destruction of the free radicals. Data for the formation of lysozyme dimers on irradiation have been obtained[91] by pulse radiolysis (with recording of light scattering), the dimerisation rate constant amounting to 10^6 litre $mole^{-1}$ s^{-1}. If it is assumed that the formation of the dimers is the result of the recombination of the lysozyme macroradicals, then the above quantity must be regarded as the lower limit to the rate constants for the recombination of the macroradicals. This quantity is sufficient to explain the presence of slow components, but is too low to account for the rapid exponential components. The macroradicals most probably decompose with elimination of low-molecular-weight radicals and a cross-disproportionation. In the case of peroxy-macroradicals there is a possibility that the latter decompose with formation of O_2^-.

There exists yet another explanation of the exponential kinetic curves for the destruction of radicals—it involves the immediate formation of a pair of radicals on one macromolecule separated by a fairly short distance. This situation may obtain on irradiation of proteins with u.v.light.

In the presence of oxygen in the system, peroxy-macroradicals are formed. It is difficult to investigate them by direct methods, but there exists an extensive literature on the reactions and transformations of low-molecular-weight peroxy-radicals whose structures are similar to those of the radicals derived from the protein and DNA groups (see, for example, Timofeev-Resovskii et al.[25] and Kayushin et al.[60]).

The construction of a possible mechanism of the oxidation processes is the aim of a quantitative or at least a semi-quantitative description of the experimental data within the framework of a simplified kinetic scheme. The proposed schemes must explain the yields of the oxidation and product formation reactions and the kinetics of the decomposition of the groups of the macromolecules and of the accumulation of the modified products. The formulae obtained must be consistent with the dependence of the rate of oxidation on the dose rate, temperature, the concentrations of the substrate oxidised, oxygen, and various additives, pH, ionic strength, viscosity, etc.

A simplified kinetic scheme for the secondary free-radical reactions involving biomacromolecules is presented below.[78-98]

Scheme 1

$$B \xrightarrow{h\nu,\ O} \dot{R}\,(\dot{R},\ \dot{R}^+,\ R^-),\ O_2^-\,(H\dot{O}_2)\,, \qquad (I)$$

$$\dot{R} \xrightarrow{k_1} \ldots P_i\,, \qquad (II)$$

$$\dot{R} + O_2 \xrightarrow{k_2} R\dot{O}_2\,, \qquad (III)$$

$$R\dot{O}_2 + O_2^- \rightarrow \Pi + O_2\,, \qquad (IV)$$

$$R\dot{O}_2 \rightarrow P_i + O_2^- + H^+\,, \qquad (V)$$

$$2R\dot{O}_2 \rightarrow P_i + O_2\,, \qquad (VI)$$

$$2O_2^- \xrightarrow{2H^+} H_2O_2 + O_2\,, \qquad (VII)$$

$$R\dot{O}_2 + B \rightarrow \Pi + \dot{R}\,(R\dot{O}_2 \cdots HR \rightarrow \Pi + \dot{R})\,, \qquad (VIII)$$

$$\dot{R} + O_2^- \rightarrow \Pi\,, \qquad (IX)$$

$$R^- + O_2 \rightarrow \dot{P}_i + O_2^-\,, \qquad (X)$$

$$\Pi \rightarrow P_i\,, \qquad (XI)$$

where B is a biomacromolecule, $\dot{R}$ is a generalised representation of many types of macroradicals, RO_2 are peroxy-macroradicals, Π are stable or labile peroxides, and P_i is a generalised representation of the reaction products.

In the kinetic scheme considered, reaction (I) represents the primary processes involving the formation of free radicals of different types and the O_2^- radical-anion in the system. Reactions (II) and (III) are competing reactions of free macroradicals, while peroxy-macroradicals are formed in reaction (III). Reaction (IV) represents the cross-disproportionation of peroxy-radicals and superoxide radical-anions. It is noteworthy that the participation of O_2^- in the radiation-induced and photochemical oxidation of peptides and proteins has been discovered by the addition of superoxide dismutase, $O_2^- + O_2^- \xrightarrow{2H^+} H_2O_2 + O_2$.[93,94] The rate constant for reaction (IV) is about 10^9 litre $mole^{-1}$ s^{-1}. A process involving the additional formation of superoxides, namely reaction (V), has been proposed to account for data for the radiation-induced oxidation of proteins and DNA.[36,37] Reactions (VI) and (VII) are the usual radical disproportionation reactions.

Reaction (VIII) has been introduced to explain the relatively high yields in the absorption of oxygen, which exceed the yields in the formation of radicals when proteins and DNA interact with hydroxy-radicals. It has been suggested that this reaction proceeds via an intramolecular mechanism. Reactions (IX) and (X) are possible. It is noteworthy that reaction (IX) can proceed also in the presence of a deficiency of oxygen. Finally, the peroxides formed in reaction (IV) can decompose with formation of a wide variety of products.

The rates of the radiation-induced oxidation of proteins and DNA depend only slightly on temperature, which is consistent with Scheme 1, and only reaction (VIII) can have an activation energy greater than 10 kcal mole^{-1}, while the remaining reactions are characterised by lower activation energies. Within the framework of Scheme 1, the yield of peroxides and the absorption of oxygen should depend only insignificantly on the irradiation dose rate and should be determined by the competition between reactions (IV) and (VII), which has in fact been observed experimentally.[14,38,76,83,93-98]

For many compounds (serum albumins, trypsin, glycyltryptophan), the dependence of the rate of photochemical and radiation-induced oxidation on the oxygen concentration is described by the formula[95-98]

$$y = \frac{\omega}{\omega_{p=1}} = \frac{p(a_1 + 1)}{a_1 + p} , \qquad (1)$$

where ω is the rate of oxidation at a given oxygen concentration, $\omega_{p=1}$ the rate of oxidation in air, p the relative concentration of oxygen, and a_1 a parameter whose value is in the range 0.01–0.1. Within the framework of Scheme 1, the parameter a_1 is given by

$$a_1 = \frac{k_1}{k_2 O_2^{air}} ,$$

If it is assumed that $k_1 = 10^3$ s^{-1} and $k_2 = 10^8$ litre mole^{-1} s^{-1} (Table 4) and that the concentration of oxygen in water exposed to air at 25 °C is 2.6×10^{-4} M, then the calculated parameter a_1 is 0.04, a value which is comparable to that found experimentally.[95,98]

V. THE PRIMARY PROCESSES IN THE RADIATION-INDUCED OXIDATION

The formation of the hydroxy-radical, the hydrated electron, and the hydrogen atom when water is exposed to ionised radiation is the result of a series of physical and chemical processes which we shall not consider here. Free radicals are formed initially in tracks, spurs, and blobs and their distribution in space is extremely non-uniform. This non-uniformity and the inhomogeneity of the initiation should be taken into account in some way, but we do not possess the relevant experimental data. We shall therefore assume that the formation of the active water radiolysis products is fairly uniform.

The rate constants for the reactions of macromolecules with $\dot{H}$, $\dot{O}H$, and $\bar{e}$, presented in Section III, are close to the diffusion-dependent values. This actually implies that at protein and DNA concentrations of the order of 10^{-4} M the active radiolysis products are captured by these substrates; at concentrations of the order of 10^{-5} M there is no point in taking into account the cross reactions of the radiolysis products, since the rates of their reactions with biopolymers are much higher. In the presence of oxygen, the hydrated electron and the hydrogen atom do not participate in the oxidation process, but superoxides and hydroxy-radicals remain active:

$$2\dot{O}H \rightarrow H_2O_2 ,$$
$$2O_2^{\bar{}} \xrightarrow{2H^+} H_2O_2 + O_2 ,$$
$$O_2^{\bar{}} + \dot{O}H \xrightarrow{H^+} H_2O + O_2 .$$

It is easy to show that the third reaction makes the greatest contribution to the destruction of hydroxy-radicals. In order to simplify the kinetic calculations, it was useful to introduce formally a linear destruction reaction [reaction (XIII)] of hydroxy-radicals which are destroyed both in the reactions described above and in the interactions with impurities.

Taking into account these considerations, a simplified scheme for the primary processes involving the formation of macroradicals when biopolymers (B) are exposed to radiation is presented below:[92-103]

Scheme 2

$$H_2O \xrightarrow{h\nu} \dot{O}H, \bar{e} , \qquad (XII)$$

$$\dot{O}H \xrightarrow{k_3} H_2O_2, H_2O , \qquad (XIII)$$

$$\dot{O}H + B \xrightarrow{k_4} \dot{R} , \qquad (XIV)$$

$$\bar{e} + B \rightarrow R^{\bar{}} , \qquad (XV)$$

$$\bar{e} + O_2 \rightarrow O_2^{\bar{}} . \qquad (XVI)$$

At a fairly high oxygen concentration reaction (XV) may be disregarded and we obtain the following expression for the dependence of the relative rate of oxidation z on the concentration of the substance oxidised c:

$$z = \frac{\omega}{\omega_\infty} = \frac{c}{a_2 + c} , \qquad (2)$$

where $a_2 = k_3/k_4$, ω is the rate of oxidation, and ω_∞ the rate of oxidation at $c \rightarrow \infty$. Relations of this type have been known for a long time.[99] They describe satisfactorily the concentration variation for many low-molecular-weight substances and synthetic and natural polymers, including proteins and DNA. Since the rate constant k_3 is not elementary, relations of type (2) do not carry significant information about the oxidation process, but deviations from them in the radiolysis of aminoacids, sugars, and other substances are of interest.[100,101]

The unusual dependence of the gamma-chemiluminescence of solutions of glycyltryptophan on the peptide and oxygen concentrations made it necessary to consider the hypothetical $H\dot{O}_3$ species[96]—the acid analogue of the ozonide radial-ion $O_3^{\bar{}}$.

The influence of hundreds of substances on the radiation-induced reactions of proteins and nucleic acids have been investigated. Such studies had in the main two aims—the elucidation of the mechanisms of the radiation-induced reactions of macromolecules and the establishment of rapid tests for the preliminary testing and selection of potential protectors and sensitisers. The introduction of a fourth initial component into a system containing water, the polymer, and oxygen greatly complicates the system and makes it difficult to describe the experimental data within the framework of simple kinetic schemes. In many cases, it is possible to take the fourth substance into account. The acceptor introduced can interact with all types of active species involved in the radiation-induced oxidation: the active products of the radiolysis of water, the free radicals of the biopolymer, the peroxy-radicals, and the peroxides; the reactions of the acceptor entail the appearance in the system of new radicals

derived from the acceptor, which can also react with macromolecules. The introduction of the acceptor (A) leads to a whole set of reactions:

$$\dot{O}H + A \rightarrow \dot{R}_A , \qquad (a)$$

$$\bar{e} + A \rightarrow R_A^{\cdot -} , \qquad (b)$$

$$O_2^{\cdot -} + A \rightarrow R_A^{\cdot -} + O_2 , \qquad (c)$$

$$\dot{R} + A \rightarrow \dot{R}_A + P_i , \qquad (d)$$

$$R\dot{O}_2 + A \rightarrow \dot{R}_A + \Pi , \qquad (e)$$

$$\Pi + A \rightarrow P_i . \qquad (f)$$

All these reactions inhibit to some extent the radiation-induced oxidation of proteins and nucleic acids. Naturally reactions (a) and (d) make the greatest contribution to the protection. A series of protectors of the type of cysteamine and cysteine act in accordance with this mechanism. The rate constants for their reactions with all types of active species are fairly large and these substances give rise to free radicals which are relatively inactive.[102]

The acceptor free radicals $\dot{R}_A$ react with biopolymers at sufficient concentrations of the latter to form macroradials:

$$\dot{R}_A + B \rightarrow P_A + \dot{R} , \qquad (g)$$

where P_A are the acceptor reaction products. There is a possibility of the competing reaction

$$\dot{R}_A + O_2 \rightarrow R_A\dot{O}_2 . \qquad (h)$$

Judging from the available data,[97,102,103] such protective effects with latent sensitisation have been observed for solutions of biopolymers and even for living cells when alcohols and other substances, which react effectively with hydroxy-radicals to form fairly active acceptor free radicals, are introduced. The rate constants for the reactions of alcohol radicals with proteins are close to the diffusion-dependent values,[103] the oxy-radicals being the most reactive; effects unusual for free radical reactions are observed: the more hydrophobic the alcohol radical, the more readily it penetrates the hydrophobic "gaps" in the protein macromolecules.

Effects of explicit radiosensitisation have been observed for proteins, nucleic acids, and whole cells.[5,6,11,12] As a rule substances, the rate constants for the reactions of which with hydrated electrons are high, exhibit a sensitising activity. Several sensitisation pathways have been proposed, the simplest of which involves the formation of an acceptor radical-anion via reaction (b) and the formation of a macroradical in the reactions with biopolymers:

$$R_A^{\cdot -} + B \rightarrow \dot{R} + P_A . \qquad (i)$$

There are many competing pathways leading to the destruction of acceptor radical-anions, namely the reactions with oxygen, disproportionation, etc.

VI. KINETIC SCHEME FOR SENSITISED PHOTOCHEMICAL OXIDATION

Studies on the degrative effect of "near" u.v.light and visible light on living organisms have recently become more vigorous and the problem of protection against such damage and its prophylaxis has arisen.[14,104] When light acts on solutions of sensitisers, numerous reactions of their electronically excited states and free radicals, radical-ions, and peroxides take place in the presence of oxygen and lead to the degradation of the sensitiser molecules. Naturally there are many sensitisation mechanisms. A triplet–triplet energy transfer from acetone, acetophenone, and benzophenone to the DNA bases has been observed.[105,106] It involved the formation of cyclobutane dimers and breaks in the DNA chain were also observed. In the presence of oxygen the amount of dimer diminished, but the number of breaks increased. In photochemical oxidation this sensitisation pathway is probably fairly rare. Here we shall consider a possible but extremely simplified mechanism of the photochemical oxidation of macromolecules. The probable kinetic scheme for the primary processes is indicated below:

Scheme 3

$$S \xrightarrow{h\nu} {}^3S \qquad (XVII)$$

$${}^3S + S \xrightarrow{k_5} S + S, \qquad (XVIII)$$

$${}^3S + O_2 \xrightarrow{k_6} S + O_2, \qquad (XIX)$$

$${}^3S + O_2 \xrightarrow{k_7} S + {}^1O_2, \qquad (XX)$$

$${}^3S + B \xrightarrow{k_8} S + B, \qquad (XXI)$$

$${}^3S + B \xrightarrow{k_9} R + CH, \qquad (XXII)$$

$$\dot{C}H + O_2 \rightarrow S + O_2^{\cdot -} + H^+, \qquad (XXIII)$$

$${}^1O_2 \xrightarrow{k_{10}} O_2 , \qquad (XXIV)$$

$${}^1O_2 + B \xrightarrow{k_{11}} \Pi , \qquad (XXV)$$

where S is a sensitiser molecule in the ground state and ^3S the triplet electronically excited state of the sensitiser. The triplet state of the sensitiser can be quenched physically in reactions (XVIII)–(XXI), reaction (XXII), involving the formation of singlet oxygen, being the most important. Reaction (XXII) involves formation of free radicals from the macromolecules via a dehydrogenation or charge transfer mechanism and reaction (XXIII) represents the regeneration of the sensitiser. Reaction (XXIV) is the deactivation of singlet oxygen and reaction (XXV) involves the addition of singlet oxygen to the macromolecule. On the basis of the kinetic Scheme 3, subject to the condition that the concentrations of all types of active species are quasi-stationary, an expression has been obtained for the rate of oxidation ω:

$$\omega = \frac{a_0\omega_T cp\,(a_3 + a_4 p + c + a_7)}{(a_1 + p)\,(a_3 + c)\,(a_5 p + c + a_6)} ,$$

where ω_T is the rate of formation of triplet excited states of sensitiser:

$$a_0 = \frac{k_9}{k_8 + k_9}, \quad a_3 = \frac{k_{10}}{k_{11}}, \quad a_4 = \frac{k_7 O_2^{air}}{k_9},$$

$$a_5 = \frac{(k_6 + k_7)\,O_2^{air}}{k_8 + k_9}, \quad a_6 = \frac{k_5}{k_8 + k_9}, \text{ and } \quad a_7 = \frac{k_1 k_7}{k_2 k_9}$$

In the presence of a fairly high oxygen content ($p > 0.1$), the term a_1 may be neglected and apparently so can the parameter a_7, which simplifies the formulae. We shall consider special cases. At a high oxygen concentration, the dependence of the relative rate of the concentration of macromolecules is given by:

$$z = \frac{c}{a_3 + c} \quad (3)$$

Relations of this type have been observed for many systems: glycyltryptophan, in the presence of xanthene dyes, psoralen, and other sensitisers, and trypsin with sensitisation by eosin and retinal.[107-112]

When there is no generation of singlet oxygen, the concentration dependence simplifies:

$$z = \frac{c}{a_5 p + a_6 + c} \quad (4)$$

It may be assumed that this type of relation obtains in the systems glycyltryptophan–ketones, human serum albumin–riboflavin, and bovine serum albumin–anilinonaphthalenesulphonate (ANS).[107,111]

The dependence of the relative rate of oxidation on the relative oxygen concentration has a by no means simple form:

$$y = \frac{a_6 + a_5 + c}{a_3 + a_5 p + c} \cdot \frac{a_3 + a_4 p + c}{a_3 + a_4 + c} \quad (5)$$

For an experimental confirmation of a relation of this type, it is necessary to have numerous data with wide-scale variation of the concentrations of the substrate oxidised and of oxygen. Such studies have been performed in two systems: glycyltryptophan–eosin and trypsin–eosin.[108,110] So far as we are aware, studies of this kind on DNA have not been performed. Finally, when the contribution of singlet oxygen to the photochemical oxidation is low, the dependence on the oxygen concentration assumes the following form:

$$y = \frac{a_6 + a_5 + c}{a_6 + a_5 p + c} \quad (6)$$

It is seen from Eqn.(6) that the relative rate of photochemical oxidation falls with increasing oxygen concentration. This type of dependence has been observed for the human serum albumin–riboflavin system.[107] The parameters a_3, a_4, and a_5 have been determined from the experimental data presented above, which made it possible to estimate certain rate constants and their ratios (Table 5). The rate constants for the reactions of singlet oxygen with a series of peptides and proteins are close to the diffusion-dependent values. The quenching of triplet electronically excited states by proteins is also extremely effective. The quanitity $(k_6 + k_7)/(k_8 + k_9)$ characterises the efficiency of the quenching of triplet excited states of sensitisers by oxygen relative to the quenching by proteins and peptides; for proteins, the above quantity is of the order of unity. The ratio k_7/k_9 characterises the relative efficiency of the formation of singlet oxygen and of its involvement in the oxidation in relation to the formation of protein free radicals; Table 5 shows that the pathway involving singlet oxygen predominates.

VII. PHOTOPHYSICAL AND PHOTOCHEMICAL REACTIONS OCCURRING WHEN MACROMOLECULES ARE ACTED UPON BY ULTRAVIOLET RADIATION

The photophysical processes in proteins have been studied in much greater detail than in DNA. This is associated with the high luminescence yields in proteins and the insignificant luminescence yield in DNA molecules. The photochemical reactions in these systems are also different. Whereas approximately the same products are formed in the case of proteins as on exposure to ionising radiation and the photochemical oxidation proceeds with formation of free radicals, the main product of the photochemical reactions of DNA is cyclobutane dimers, while the yields of the remaining products are low. The dimers are fairly readily destroyed by enzymic repair systems, which ultimately lead to a very high photostability of the DNA molecule in living cells. The appearance of photobiological effects requires u.v. radiation doses, in terms of the energy absorbed by the cell nuclei, higher by 2–3 orders of magnitude than on exposure to ionising radiation.[14,17,100] A simplified scheme for the photochemical oxidation of proteins is given below:

Scheme 4

$$B \xrightarrow{h\nu} {}^1B, \quad (XXVI)$$

$${}^1B \rightarrow B, \quad (XXVII)$$

$${}^1B \rightarrow {}^3B, \quad (XXVIII)$$

$${}^3B \rightarrow B, \quad (XXIX)$$

$${}^3B + O_2 \rightarrow B + O_2, \quad (XXX)$$

$${}^3B + O_2 \rightarrow B + {}^1O_2, \quad XXXI)$$

$${}^1B \rightarrow P_i, \quad (XXXII)$$

$${}^3B \rightarrow P_i, \quad (XXXIII)$$

$${}^1B \rightarrow [{}^1B^{\cdot} \ldots \bar{e}] \rightarrow \dot{R}^{\cdot} + \bar{e}, \quad (XXXIV)$$

$${}^3B + B \rightarrow \dot{R}H + \dot{R}, \quad (XXXV)$$

$${}^3B \rightarrow \dot{R} + \dot{H}(\bar{e} + H^+), \quad (XXXVI)$$

$${}^3B + O_2 \rightarrow \dot{R}^+ + O_2^{\bar{}}, \quad (XXXVII)$$

$$[{}^1B^+ \ldots \bar{e}] + O_2 \rightarrow \Pi, \quad (XXXVIII)$$

$$\Pi \xrightarrow{h\nu} P_i, \quad (XXXIX)$$

where reactions (XXVI)–(XXXI) are the usual photophysical reactions.

Table 5. The rate constants and their ratios for the sensitised photochemical oxidation reactions of a number of substances and the constants calculated within the framework of thekinetic Schemes 1 and 3 from the literature.[98,107-112]

Substance	Sensitiser	$10^{-9} k_1$, litre mol^{-1} s^{-1}	$10^{-9}(k_8 + k_9)$, litre mol^{-1} s^{-1}	$\frac{k_6 + k_7}{k_8 + k_9}$	k_7/k_9
Glycyltryptophan	Eosin	1.1	1	27	6.2
Ditto	Uranin	1.2	—	—	—
»	Psoralen	1.1	—	—	—
»	Nicotinic acid	1	—	—	—
»	Acetone	—	1	8.6	—
Trypsin	Eosin	8.6	3	1	3.8
Ditto	Uranin	8	—	—	—
»	Retinal	6.4	—	—	—
Human serum albumin	Eosin	21	—	—	—
Ditto	Riboflavin	—	4.8	0.54	—
Bovine serum albumin	ANS	—	4	0.75	—

The principal chromophores in proteins are tryptophan, tyrosine, and phenylalanine; the fluorescence yields of these molecules in neutral aqueous solutions are 23, 21, and 3.8% and the lifetimes of the singlet electronically excited states are 3.1, 3.3, and 5.3 ns respectively.[113-115] The

fluorescence yields for tryptophan-containing proteins are 1–30%, the lifetime of the singlet electronically excited state is 1–6 ns, and the yield of the triplet electronically excited states is up to 10%.[113,114,116–118] In photochemical oxidation oxygen is absorbed with a quantum yield of 0.5–2%, the tryptophan residues decompose with a yield of 1–2%, and enzymes are inactivated with yields of 0.1–3%.[113–120]

The fluorescence quantum yield in DNA is extremely low (10^{-3}–10^{-4}%) and the lifetimes of the singlet electronically excited states are 1–5 ps.[121] The yield of the dimers reaches 4% and on exposure to irradiation by a laser the number of single breaks and other defects increases.[32,122,123] It has been suggested that dimers may be formed with participation of both singlet and triplet electronically excited states—reactions (XXXII) and (XXXIII). The main bulk of these defects are probably formed with participation of singlet excited states, because oxygen does not interfere with dimerisation. There are insufficient experimental data to examine the possible DNA photochemical oxidation processes.

It has come to be assumed that the main reaction occurring in the irradiation of proteins with light at wavelengths in the range 260–300 nm is photoionisation with participation of singlet electronically excited states in the aromatic groups of the protein—reaction (XXXIV), which includes the formation of a complex with partial charge transfer. This reaction proceeds via a one-quantum mechanism in liquid aqueous solutions and via a two-quantum mechanism in frozen solutions.[34,113,116–119,124,125]

Reaction (XXXIV) results in the formation of a radical-cation and a hydrated electron. Other possible reactions leading to the formation of free radicals are also considered in the literature quoted.

Reaction (XXXV) represents the abstraction of hydrogen atoms in the reactions of triplet excited states of the aromatic groups of the protein with neighbouring groups in the macromolecule to form a pair of free radicals and, finally, reaction (XXXVI), which represents the formation of hydrogen atoms or photoionisation with participation of triplet electronically excited states of aromatic groups, is relatively unlikely, being energetically unfavourable.

It has usually been assumed that reaction (XXXI), involving the formation of singlet oxygen, is relatively ineffective in the case of proteins, although there is no evidence for this. We believe that this contribution to photochemical oxidation may prove to be significant.

In constructing a photochemical oxidation mechanism, account is taken of reaction (XXXVII)—the formation of the radical-cation derived from the aromatic groups and of the superoxide radical-anion. This reaction probably occurs in the photochemical oxidation of free tryptophan and peptides containing tryptophan. In order to determine the contribution of the superoxide, experiments have been performed[93,94] in which superoxide dismutase was added during the photochemical oxidation of glycyltryptophan. The enzyme inhibits sharply the formation of unstable peroxides, which indicates a significant contribution of the superoxide to the oxidation. In the case of proteins the addition of the enzyme reduces the yield of peroxide by only 20–30%, i.e. O_2^- is only partly released into space and a "latent radical" mechanism involving the formation of radicals, possibly via reaction (XXXVIII), operates. Oxygen reacts either with the complex in the excited state or with groups in the protein in the triplet excited state, forming peroxides directly. In dilute solutions, at a low optical density, unstable peroxides undergo photochemical decomposition [reaction (XXXIX)].

Thus examination of questions associated with the action of u.v. light on proteins and DNA leads to the conclusion that their reactions follow different pathways: in the case of proteins a free-radical mechanism of the formation of damage-induced defects operates, while in the case of DNA the reactions of free radicals are not important.

VIII. THE POSSIBLE REDISTRIBUTION PROCESSES INVOLVING THE INITIAL DAMAGE-INDUCED DEFECTS IN MULTICOMPONENT SYSTEMS CONTAINING DNA, PROTEINS, AND OTHER SUBSTANCES

The main target when living cells are acted upon by ionising radiation is the cell nuclei or more precisely the DNA molecules. The biochemical composition of the cell nuclei is extremely varied and the principal component consists of a wide variety of proteins. The protein : DNA ratio in different cells varies within broad limits,[126–128] such data being presented in Table 6. Proteins can perform a wide variety of biochemical functions and are effective acceptors of all types of active species. Tables 3 and 4 present the estimated rate constants for different reactions. Proteins and DNA interact effectively with the active water radiolysis products and the free radicals derived from DNA can react with proteins. In qualitative terms, it is understandable that the higher the protein concentration, the smaller the damage to DNA. Here we shall make an attempt to estimate the contribution of proteins to the radiation stability of DNA.

We shall consider a simplified kinetic scheme for the processes occurring in the protein–DNA system on irradiation in aqueous solution. We shall take into account only the reactions of hydroxy-radicals with the macromolecules and DNA:

$$H_2O \xrightarrow{h\nu} \dot{O}H,\ \bar{e},\ \dot{H}\ ,$$

$$\dot{O}H + B \xrightarrow{k_1'} \dot{R}_1\ ,$$

$$\dot{O}H + D \xrightarrow{k_2'} \dot{R}_2\ ,$$

where $\dot{R}_1$ and $\dot{R}_2$ are protein and DNA free radicals respectively. The macroradicals could enter into numerous reactions, including the following:

$$\dot{R}_1 + D \xrightarrow{k_3'} B + \dot{R}_2,$$

$$\dot{R}_2 + B \xrightarrow{k_4'} D + \dot{R}_1.$$

Finally we have the destruction of radicals leading to chemical modification:

$$\dot{R}_1 \xrightarrow{k_5'} P_1\ ,$$

$$\dot{R}_2 \xrightarrow{k_6'} P_2\ ,$$

where P_1 and P_2 are the modification products.

The contribution of the reaction with k_3' to the degradation of DNA can be hardly large, because the protein free radicals are not very active and the absolute DNA concentration in the nucleus is low. Subject to the condition that the concentrations of all the active species are quasi-stationary, the rate of degradation of DNA ω_D is given by

$$\omega_D = \frac{k_2'k_6'[D]\omega}{(k_6' + k_4'[B])(k_1'[B] + k_2'[D])},$$

where ω is the rate of formation of hydroxy-radicals. We introduce the variable $x' = [B]/[D]$ and obtain the following equation for the relative radiation stability of DNA (y'):

$$y' = \frac{\omega}{\omega_D} = (a_1'x' + 1)(a_2'x' + 1)\ , \qquad (7)$$

where

$$a_1' = \frac{k_1'}{k_2'} \quad a_2' = \frac{k_4'[D]}{k_6'}\ .$$

The parameters were estimated from the rate constants (Tables 3 and 4) and the DNA concentration (approximately 4×10^{-4} M). The quantity a'_1 varies in the range 0.1–1 and $a'_2 = 0.05$–0.2. If it is assumed that $a'_1 = 0.5$ and $a'_2 = 0.1$, we obtain from Eqn.(7)

$$y' = (0.5\,x' + 1)\,(0.1\,x' + 1) \qquad (8)$$

Table 6 presents the results of the calculation by Eqn.(8) and it is seen that the stability of DNA increases sharply with increase of the protein : DNA ratio. According to radiobiological data, the stability of cells increases in the same sequence.[4,18,21,25]

Table 6. The radiation stability (y') of DNA as a function of the "protein : DNA" ratio in the cell nuclei of a number of organs and tissues.[126–128]

Object	Protein : DNA	y'
Lymphocytes	2.8	3.1
Thymus	3	3.3
Bone marrow	3.3	3.5
Spleen	6.3	7
Small intestine	8.7	10
Lungs	11.2	14
Kidney	16.7	24.8
Liver	23.4	42.5
Brain	24.6	46
Heart	55.6	188

Remarks: The quantity y' was calculated by Eqn.(8) for a homogeneous solution of the protein and DNA at concentrations comparable to those within the cell nuclei, the stability of DNA in the absence of protein being adopted as unity.

Table 7. The average concentrations (c) and the effective first-order rate constants (k) for the reaction of the components of cell nuclei and membranes with singlet oxygen.

Substance	c, M	k, s^{-1}
Nuclear proteins	$3 \cdot 10^{-3}$	$3 \cdot 10^{6}$—$3 \cdot 10^{7}$
Nuclear DNA	$4 \cdot 10^{-4}$	4
Membrane proteins	10^{-2}	10^{7}—10^{9}
Membrane lipids	1	10^{3}—10^{5}
Inhibitors of the type of tocopherol	10^{-3}	10^{2}—10^{4}

Remarks: k is the product of the rate constant for the reaction of a given substance with singlet oxygen and the concentration of the latter (Table 3).

When the known protector cysteamine is introduced into the system (Tables 3 and 4), its competing reactions with hydroxy-radicals and the DNA free radicals are included in the system. Fairly effective protection can be achieved at protector concentrations of the order of 10^{-3} M, which is comparable to the concentrations giving rise to an effect in a radiobiological experiment.[129] Naturally, the formal kinetic results make it possible to estimate the degree of primary protection of DNA by the protein in solution and cannot claim to be able to account for the complex final biological results of the action of radiation.

Table 3 presents certain data for the reactions of singlet oxygen, which permits a rough estimation of the redistribution of damage-induced defects in multicomponent systems in sensitised photochemical oxidation involving such oxygen. Table 7 also presents estimates for the components of cell nuclei and membranes. It shows that the effective rate constants for the first-order reactions of cell components with $^1O_2$ are higher by several orders of magnitude for proteins than for the remaining components, i.e. proteins are the main target.

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Data concerning the mechanisms of the action of radiation on proteins and nucleic acids are of significant interest from the standpoint of the control of the biological consequences of such influences in the primary physicochemical stages of the initial damage. It is seen from the results presented that numerous intermediates participate in the photochemical reactions of biopolymers—electronically excited states, radical-ions, free radicals, peroxy-radicals, and peroxides, as suggested by N.M.Emanuel' in the 1950's. In a number of cases the experimental data can be described within the framework of simplified kinetic mechanisms with participation of a small number of active species. Kinetic equations have also shown that the damage to the "main" DNA molecule can be greatly reduced in the presence of protein—the principal component of cell nuclei.

The complexity of the composition and structure of proteins and nucleic acids preclude the detection of all the reactions leading to the chemical modification of the primary structure of the biomacromolecules and the majority of the mechanisms proposed are tentative. All this indicates the necessity of further studies of these systems using modern methods for the determination of intermediate and final reaction products.

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New Aspects of the Application of Nuclear Magnetic Resonance to the Study of Chemical Exchange Processes

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The application of the analysis of the total line shape (ATLS) in dynamic NMR to the investigation of complex chemical exchange is examined. Theoretical aspects of this problem, illustrated in relation to the available experimental data, are described. The methodological problems of dynamic NMR are discussed: the sources of error and the role of the medium, the interpretation of the activation parameters $\Delta H^{\neq}$, $\Delta G^{\neq}$, and $\Delta S^{\neq}$, and also the new varieties of the method and their applications.
The bibliography includes 171 references.

CONTENTS

I. Introduction 931
II. NMR in systems with chemical exchange. Problems of the analysis of the total line shape 932
III. Special methods 941

I. INTRODUCTION

Since the publication of the first fundamental studies,[1-6] numerous reviews and monographs surveying the results of kinetic studies by the NMR method have appeared. General information can be found in a series of publications.[7-17] A more detailed description of the principles of the theory, method, and applications can be found in reviews.[18-24] The bibliography of the publications in 1970–1974 can be found in a periodical publication.[25] The appearance in 1975 of a fundamental collected volume[26] of review articles on all the most important problems of dynamic NMR (DNMR) heralded the completion of the first stage of its development and establishment. The review articles in the following period were devoted to special problems: dynamic ^{13}C NMR spectroscopy[27] and its application to the study of the dynamics of metal carbonyl[28] and cyclic organic[29] compounds, the application of the methods for the analysis of the total line shape to the examination of the chemical exchange mechanism,[30] and the physical aspects of the theory based on the influence of chemical exchange on relaxation processes[31] and the study of "rapid kinetics".[32] Special mention should be made of the publication of the first book on the general theory of the NMR of chemically exchanging systems[33] and the first monograph devoted to the methodological aspects of DNMR.[34]

Several varieties of the DNMR method are known. The non-selective pulse NMR is an independent method both as regards theory and the procedure used to obtain spectroscopic and kinetic data and as regards experimental technique. The principles of its application to kinetic studies have been described.[35]

Modern NMR Fourier spectrometers make possible experiments under both stationary and selective pulsed conditions. The use of the relaxation times T_1 and T_2, corresponding to the nuclear transitions between individual energy sublevels,

together with the chemical shift δ and the spin–spin coupling constant J, has therefore become a common feature of combined studies of chemical systems. The same universality is to be expected in kinetic investigations in the immediate future.

The DNMR method in the stationary regime is used in the range of reaction rate constants 10^{-1}–10^5 s^{-1} (^1H NMR). Selective pulse methods not only significantly expand the above range (in certain cases from 10^{-3} to 10^6 s^{-1}) but sometimes can yield unique information about the mechanisms of complex chemical exchange processes. It has now become possible to carry out kinetic studies at an extremely low concentration of magnetic nuclei (in gases, in solutions at infinite dilution but with a high natural abundance of magnetic nuclei in the specimen, by ^{13}C and ^{15}N NMR without enrichment in the usual solutions, etc.).

The applications of NMR to kinetic studies are extremely varied and numerous. A fairly completely survey of the research carried out in recent years can be given only within the framework of a collected volume analogous to that of Jackman.[26]

In the present review we shall consider new aspects of the application of NMR to the study of systems with a complex chemical exchange as well as the scope and applications of the new special methods. The most important publications of recent years will be mostly quoted. Brief information about the studies published in 1979–1983 can be found in the periodical reference publication.[36]

II. NMR IN SYSTEMS WITH CHEMICAL EXCHANGE. PROBLEMS OF THE ANALYSIS OF THE TOTAL LINE SHAPE

1. Principal Postulates of the Theory. Multiparameter Exchange. Difficulties and Limits of Applicability

The most interest and most important field in which analysis of the total NMR line shape is used in systems with chemical exchange (ATLS DNMR)† involves the study of the mechanisms of intramolecular and intermolecular exchange in chemical systems where the number of exchanging sites is greater than two and the transitions between them are characterised by different rate constants. Although the theory describing the effect of chemical exchange on NMR spectra has been established in a general form, in the interpretation of the temperature variation of the spectra and in the analysis of kinetic and activation parameters for the chemical exchange serious difficulties are encountered, which are probably not always surmountable. The study of such problems has not been reflected in the review articles quoted above.

The general postulates of the theory for many-sided exchange in systems where there is no direct spin–spin coupling of the nuclear spins have been formulated within the framework of a stochastic theory.[3,4] In another approach[5] modified Bloch equations are used. In a general form the theory has been described by Reeves and Shaw.[37] A detailed discussion of this question can be found in Johnson's[18] and Swift's[31] books and we shall confine ourselves only to brief remarks.

We shall consider a set of magnetic nuclei which can execute random jumps between n different magnetic environments (equilibrium positions). We shall characterise these magnetic environments by a set of Larmor precession frequencies ω_r and spin–spin relaxation times $^*T_{2r}$ (which do not take into account the effects of chemical exchange). The subscript r denotes the equilibrium position ($r = 1, \ldots, n$). In terms of a rotating coordinate system, the equation describing the movement of the xy component of the macroscopic magnetisation $M_{xy} = M_x + iM_y$ in these equilibrium positions under slow pass conditions can be represented in the following general form:[34]

$$\{-{}^*T_{2r}^{-1} + i(\omega_r - \omega)\} M_{xy}^r + \sum_s K_{sr} M_{xy}^r + i\omega_1 M_0 P_r = 0 , \qquad (1)$$

where ω_1 is the angular frequency of the microwave frequency field, M_0 the equilibrium magnetisation, P_r the probability of finding the nuclei in the position r with $\sum_{r=1}^{n} P_r = 1$, $K_{rr} = -\tau_r^{-1}$, and $K_{rs} = k_{rs}$, τ_r being the resonance time of the nucleus in the position r and k_{rs} the rate constant for the transition of the nuclei from the position r to the position s; $-\sum_s k_{rs} = \tau_r^{-1}$.

On solving a system of n linear equations (1) for M_{xy} and bearing in mind that $M_{xy} = \sum_{r=1}^{n} M_{xy}^r$, it is possible to find the required function of the line form. The results of the solution of this system of equations be be conveniently represented in a matrix form. The line form function Y (for the absorption component) can then be formulated thus

$$Y \simeq \mathrm{Re}\{P \cdot [-T_2^{-1} + i(\Omega - \omega) + K^{-1} \cdot 1\} , \qquad (2)$$

where Re is the real component, K the nth order exchange matrix whose elements are the same as in Eqn.(1), T_2^{-1} and Ω are diagonal matrices with the elements $^*T_{*r}$ and ω_r, 1 is a unit column matrix, and P a row matrix with the elements P_r. This equation can be easily solved on a computer provided with a translator enabling it to operate with complex numbers.

The quantum-mechanical theory describing the influence of chemical exchange on NMR spectra was first proposed by Kaplan[6] and is based on the examination of the evolution of the density matrix for the spin systems in the Gilbertian representation (a detailed description of NMR spectra with the aid of the density matrix can be found in Lynden-Bell[20] and Slichter[38]). We shall consider briefly the main postulates of this theory.

Suppose that ψ is the wave function of a "pure" state which can be expanded in a series in terms of the basis functions Φ_n: $\psi = \sum_n C_n \Phi_n$, $p_{ij} = C_i C_j^*$. The coefficients C_i and their complex conjugates C_j^* incorporates the entire time variation of the state of the system. The average value of the physical quantity Q, to which corresponds the quantum-mechanical operator $\hat{Q}$, is defined in the form

$$\langle Q \rangle = \langle \psi | \hat{Q} | \psi \rangle = \sum_{m,k} C_m^* C_k \langle \Phi_m | \hat{Q} | \Phi_k \rangle = \sum_{m,k} p_{mk} \langle \Phi_m | \hat{Q} | \Phi_k \rangle ,$$

where the elements of the density matrix p_{mk} can be represented as a result of the action of the density matrix operator $\hat{P}$:

$$p_{km} = C_k C_m^* = \langle \Phi_k | \hat{P} | \Phi_m \rangle .$$

Then

$$\langle Q \rangle = \sum_{m,k} \langle \Phi_k | \hat{P} | \Phi_m \rangle \langle \Phi_m | \hat{Q} | \Phi_k \rangle = \sum_k \langle \Phi_k | \hat{P}\hat{Q} | \Phi_k \rangle = \mathrm{Tr}\, \hat{P}\hat{Q} = \mathrm{Tr}\, \hat{Q}\hat{P} .$$

Thus $\langle Q \rangle$ is independent of the choice of the basis functions Φ_n. The spin state of a macroscopic system such as the substance in the cavity of the NMR spectrometer consists

† The terminology is discussed in Ref.25 (1973, p.218), in Jackman's book,[26] and by Sandstrom.[34]

of a mixture of states with the corresponding wave functions and cannot be described by a single wave function. However, such a system can be described with the aid of the general system of basis functions Φ_n and the density matrix ρ with the coefficient ρ_{km} averaged with respect to the total assembly:[34]

$$\rho_{km} = \overline{C_k C_m^*} = \langle \overline{\Phi_k | \hat{P} | \Phi_m} \rangle = \langle \Phi_k | \hat{\rho} | \Phi_m \rangle .$$

Then the expected physical quantity Q averaged with respect to the assembly of systems is defined by the relation

$$\langle \bar{Q} \rangle = \mathrm{Tr}\, \hat{Q}\hat{\rho} .$$

Assuming that the Hamiltonian is the same for all the members of the assembly, the Schrödinger time equation can be written in the form

$$d\hat{\rho}/dt = \frac{i}{\hbar} [\hat{\rho}, \hat{\mathscr{H}}] . \qquad (3)$$

The wave function ψ can be represented by the product of the spatial and spin wave functions. In describing NMR, only the spin functions are considered. The basis functions for nuclei with a spin of 1/2 are the eigenfunctions α and β of the operator $\hat{I}_z$ (the z components of the spin momentum operator $\hat{I}$).

The spin-Hamiltonian for a group of identical nuclear spins can be represented in the following form in terms of a rotating coordinate system:

$$\hat{\mathscr{H}} = \hat{\mathscr{H}}_0 + \hat{\mathscr{H}}_1 = \sum_i (\nu_i - \nu) \hat{I}_{zi} + \sum_{j<k} J_{jk} \hat{I}_j \hat{I}_i + \sum_i \nu_1 \hat{I}_{xi} , \qquad (4)$$

where the subscripts i and j refer to individual spins, J_{ij} is the spin–spin coupling constant, $\nu_i = \omega_i/2\pi$, $\nu_1 \hat{I}_{xi}$ describes the interaction with the microwave frequency field H_1 having a frequency ν_1, and $\hat{I}_x$ is the x component of the spin operator $\hat{I}$.

For a description of the resonance absorption under slow pass conditions ($d\rho/dt = 0$) and in the absence of saturation and chemical exchange, it is sufficient to introduce the relaxation term $\hat{\rho}^* T_2^{-1}$ in the right-hand side of Eqn.(3):

$$i [\hat{\rho}, \hat{\mathscr{H}}] - \hat{\rho}^* T_2^{-1} = 0 . \qquad (5)$$

The resonance absorption line form is described by the function

$$Y(\nu) = \mathrm{Im} \left(\mathrm{Tr}\, \hat{\rho} \sum_i \hat{I}_i^+ \right) ,$$

where Im denotes the imaginary component of the expression in brackets, $\hat{I}^+ = \hat{I}_x + i\hat{I}_y$, and the components of the operator $\hat{\rho}$ are found from the solution of Eqn.(5).

The effects of chemical exchange are taken into account by including in Eqn.(5) the term $(\hat{\rho}^{a.e.} - \hat{\rho})\tau^{-1}$, where $\tau(k^{-1})$ is the average residence time in the equilibrium states and $\hat{\rho}^{a.e.} = \chi\hat{\rho}\chi^{-1}$. The elements of the exchange operator χ are defined in the following manner in the simplest case of mutual exchange in a system of spins of one kind:

$$\chi_{kl} = \langle \Phi_l | \hat{\chi} | \Phi_k \rangle . \qquad (6)$$

Consequently the elements of the density matrix after exchange $\rho^{a.e.}$ are given by

$$\rho_{kl}^{a.e.} = \sum_{nm} \chi_{kn} \rho_{nm} \chi_{ml} .$$

In the presence of exchange, Eqn.(5) can then be rewritten as follows:[39,40]

$$k \left(\sum_{nm} \chi_{kn} \rho_{nm} \chi_{ml} - \rho_{kl} \right) - \frac{\rho_{kl}}{{}^*T_2} + i [\hat{\rho}, \hat{\mathscr{H}}]_{kl} = 0 , \qquad (7)$$

where

$$i [\hat{\rho}, \hat{\mathscr{H}}]_{kl} = i\rho_{kl} \left\{ \sum_i (\nu_i - \nu) [(\hat{I}_z^i)_{kk} - (\hat{I}_z^i)_{ll}] + \sum_{i<j} [(\hat{I}_z^i \hat{I}_z^j)_{kk} - (\hat{I}_z^i \hat{I}_z^j)_{ll}] \right\} +$$
$$+ \frac{i}{2} \sum_{i<j} J_{ij} [\rho, \hat{I}_+^i \hat{I}_-^j + \hat{I}_-^i \hat{I}_+^j]_{kl} + i\nu_1 (\rho_{kk} - \rho_{ll}) \sum_i (\hat{I}_x^i)_{kl} .$$

Bearing in mind that $H_1 \ll H_0$, the last term in Eqn.(7) can be replaced by the constant iC.

For a description of more complex cases of chemical exchange, such as non-mutual exchange, intermolecular exchange, exchange in a system of nuclear spins of different kinds or systems with multiparameter exchange, etc., the theory based on the use of exchange operators of the type found by Eqn.(6) is inapplicable; a different definition of the elements of the density and exchange matrices is necessary. Subsequently the approach based on the use of Eqn. (3) in the Gilbertian representation was developed and applied to the analysis of the exchange effects in a wide variety of spin systems.[33,41,42]

Calculations of the line form based on Binsch's unified density matrix method,[21,43–46] in which the formulation of Eqn.(3) in terms of the Liouville representation

$$d\vec{\rho}/dt = -i\hat{\mathscr{L}}\vec{\rho}$$

proposed by Johnson[18] is used, are much more common and probably more convenient in the study of multiparameter exchange, the elements of the Liouville operator matrix are made up of the matrix elements of the spin-Hamiltonian operator for the system (in s^{-1}) in the following manner

$$L_{\mu\nu,k\lambda} = 2\pi [\mathscr{H}_{\mu k}\delta_{\nu\lambda} - \mathscr{H}_{\lambda\nu}\delta_{k\mu}] ,$$

where δ is the Kronecker delta.

Using this representation of the density matrix ρ, Binsch[43] successfully combined the possible versions of the exchange process, including intermolecular exchange.

If the system is subdivided into r non-interacting and independent subsystems, it is possible to formulate the general vector for the system $\vec{\rho}_l$ in a space l, which is the sum of the subspaces $\vec{\rho}_r$. The elements of this vector are ρ_r with the multiplier $f_r = n m_r P_r \left(\sum_r^n m_r \right)^{-1}$, where m_r is the number of nuclei (with a spin of 1/2), P_r the relative population of the subsystem r, and n the number of types of the subsystem. It is postulated that the relaxation processes and the effects of the chemical exchange can be taken into account in describing the time variation of $\vec{\rho}_l$ by including the corresponding operators $\hat{R}_l$ and $\hat{\chi}_l$ defined in the $\vec{\rho}_l$ space:

$$d\vec{\rho}_l/dt = (-i\mathscr{L}_l + R_l + \chi_l)\vec{\rho}_l \equiv M\vec{\rho}_l . \qquad (8)$$

The relaxation operator matrix R_l contains only the diagonal element ${}^*T_2$. In describing the intramolecular exchange, the exchange operator matrix χ_l can be made up of the following elements according to Alexander:[40]

$$\chi_{\mu_r \nu_r k_s \lambda_s} = \delta_{\mu k}\delta_{\nu\lambda} \left[-\delta_{\mu s} \sum_{t(\neq r)} k_{rt} + (1 - \delta_{rs}) k_{sr} \right] ,$$

where k_{sr} is the rate constant for the transition of the spin from the state s to the state r, which has the same significance as in Eqn.(1).

Under the conditions of stationary NMR, Eqn.(8) assumes the form

$$(-i\mathscr{L}_l + R_l + \chi_l)\vec{\rho}_l = 0 . \qquad (9)$$

It is more convenient to represent the operator $\hat{\mathscr{L}}$ as the sum of the operators $\hat{\mathscr{L}}_0 + \hat{\mathscr{L}}_1$; the elements of the operator $\hat{\mathscr{L}}_0$ are

made up of the elements of the Hamiltonian $\hat{\mathscr{H}}_0$ (4), describing the interaction of the spin system with the field H_0, while $\hat{\mathscr{P}}_1$ is made up of the elements of the Hamiltonian $\hat{\mathscr{H}}_1$. Eqn.(9) then becomes

$$(-i\mathscr{P}_{0l} + R_l + \chi_l)\vec{\rho}_l = i\mathscr{P}_1\vec{\rho}_l = i\vec{\sigma} \quad \text{or} \quad M_0\vec{\rho} = i\vec{\sigma} .$$

The complex magnetisation is described by the expression

$$G = (\vec{I} + \vec{\rho}_l) = i(\vec{I}^+ M_0^{-1}\vec{\sigma}) ,$$

where $\vec{I} = \sum_i I_i^+$, and $\vec{\sigma}$ for the intramolecular exchange is determined by the elements $\sigma_{\mu\nu} = CP_r\beta_{\mu\nu}$, where $\beta_{\mu\nu} = 1$ when μ and ν refer to the eigenvalues I_z differing by unity, and $\beta_{\mu\nu} = 0$ in the remaining cases. The NMR absorption function is defined as follows:

$$Y = \mathrm{Im}(G) = \mathrm{Re}(-C(\vec{I}^+[-i\mathscr{P}_{0l} + R_l + \chi_l]^{-1}\vec{\sigma})) . \qquad (10)$$

The dimension of the matrix M_0 is defined in the general case by the relation $\sum_{r=1}^{n}(2^{2m_r})$ (n is the number of equilibrium positions). However, since many elements of the vectors $\vec{I}$ and $\vec{\sigma}$ are 0, the dimension of the matrices employed diminishes to $\sum_r W_r$, where W_r is the maximum number of the possible transitions for individual systems in the position r.

In those cases where the computer is not provided with a translator for operation with complex numbers, Eqn.(10) can be solved by the method proposed by Szymanski and Gyff-Keller.[45]

Thus the solution of Eqn.(2) or (10) can yield a function describing the NMR absorption line form, which in the general case depends on several variables:

$$Y = Y(C_0, \nu_{ri}, T_{2ri}, J_{ij}^{(r)}, P_r, k_{rs}) . \qquad (11)$$

It has been suggested that the constants k_{rs} in Eqns.(2) and (11) are interdependent, which means that under this condition, with the values of k_{rs} obtained from the analysis of the line form described by Eqn.(11), is it possible to compare the true values of the corresponding activation parameters $\Delta H_{rs}^{\neq}$, $\Delta S_{rs}^{\neq}$, and $\Delta G_{rs}^{\neq}$. It is evident, as will be illustrated below, that this condition by no means always holds. The interpretation of the temperature variation of the NMR spectra of such molecules is an extremely difficult problem whose solution has not been found in a general form.

There is no doublt that a more or less successful solution of the problem is possible provided that the parameters of the NMR spectra of the partners of the exchange, which enter into the function Y, are known, i.e. when the slow exchange limit had been attained, the complete line assignment was carried out and account was taken (where possible) of the different effects influencing these parameters. The next stage involves the setting up of exchange matrices corresponding to different versions of the exchange (among the number of the possible versions, naturally excluding those which are indistinguishable spectroscopically[47]). At first sight, this problem has been exhausted and we are dealing only with computational procedures whose success is wholly determined by the complexity of the exchanging spin system and the capacity of the computer (including the adequacy of the programmes). In fact the problem is much more complicated. Eqns.(2) and (10) do not yield an unambiguous solution—even if only one version of the exchange is possible, identical line form functions can correspond to different sets of variables k_{rs}. For example, this type of ambiguity can be observed in the simplest case of the two-sided non-mutual exchange with an appreciable temperature dependence of the relative populations P_r.[48]

A rigorous solution of Eqns.(2) and (10) for many-sided exchange can be obtained when the exchange is described by a single rate constant $k_{rs} = k$ (many-sided one-parameter exchange). For such systems, the selection of a unique exchange scheme, corresponding to a real process, can be achieved by comparing the calculated and observed line forms over the entire experimental temperature range.[30] Here success depends on the extent to which the spectrum is characteristic. In the general case of multiparameter exchange the ambiguity may be either not self-evident (and in this case can probably lead to considerable errors in the determination of the activation parameters) or can be explicit and gives rise as a consequence to the problem of the interpretation of the kinetic and activation parameters.

There is no doubt that the latter problem arises only when the NMR line form is determined by several constants k_{rs}. If the spectrum can be subdivided into subspectra in which the temperature measurements correspond to any one of the processes occurring in the system, the problem reduces to the analysis of two-sided exchange, because the kinetic matrices specified by Eqns.(2) and (10) are subdivided into a series of matrices, each of which includes only one constant k. This approach has been used, for example, in the study of the simultaneous hindered rotation about four bonds in polarised ethylenes.[49] In this review we shall not discuss studies of this kind.

2. Sources of Errors. The Medium Factor. Problems of the Interpretation of the Activation Parameters $\Delta H^{\neq}$, $\Delta G^{\neq}$, and $\Delta S^{\neq}$

The problems concerning the accuracy of kinetic measurements by the NMR method have always been the subject of special attention but their importance was only fully recognised after the activation data for the main types of chemical exchange had been arranged systematically. The essential feature of this situation is strikingly illustrated by the analysis of data for the inversion of six-membered rings (cyclohexane, its *gem*-substituted derivatives, 1,3-dioxans, etc.)—one of the intermolecular exchange processes which have been investigated in greatest detail and in which "anomalies" due to the effects of the medium are least to be expected. The first most striking fact is that the error in the determination of the enthalpy of activation $\Delta H^{\neq}$ quoted in different communications varies within wide limits (from 2–3% to 20–25%). Furthermore, even for the classical cyclohexane molecule, the differences between the $\Delta H^{\neq}$ reported by different workers but obtained under similar experimental conditions (from 38.0 to 48.1 kJ mol^{-1}) greatly exceed the experimental errors quoted in the relevant communications (±0.4–1.0 kJ mol^{-1}). A selection of data can be found in a number of communications.[14,15,50,51] These factors in essence ruled out a comparative analysis, because the real effects were in most cases concealed in the actual errors of the method. There existed also the no less important problem of explaining the anomalously large negative and positive activation entropies $\Delta S^{\neq}$ (~25 e.u. for a reported accuracy to within 3–4 e.u.)[34] for a wide variety of compounds. The anomalies enumerated above are observed more strikingly in the analysis of data characterising the rotation about the partially double C–N bond in amides and related systems.[10,34,52] These anomalies, which were not explained at the time, to some extent discredited the DNMR method.

We shall briefly consider the problems relating to the mutual exchange processes for which a general analysis of the sources of experimental and computational errors has

been carried out.[34] With small stipulations, the conclusions reached can be wholly applied also to the case of non-mutual two-sided exchange.

Intramolecular exchange processes are known to be described by the Eyring and Wynn-Jones equations:[53,54]

$$\ln(k/T) = -\Delta H^{\neq}/RT + \Delta S^{\neq}/R \qquad (12)$$

$$-\Delta G^{\neq} = RT \ln \frac{kh\varkappa}{k_b T} \qquad (13)$$

Since the free energy of activation $\Delta G^{\neq}$ is determined "at a point", its values depend only slightly on the systematic errors and can be determined with a high degree of accuracy.[34,46,55,56] In precision experiments, where the temperature is determined to within not more than 0.5 K and the rate constant k is found by the ATLS method, the error of the estimate of $\Delta G^{\neq}$ may not exceed ±0.15 kJ mol^{-1}. In the standard kinetic studies, an accuracy to within a quantity of the order of 0.8 kJ mol^{-1} can be readily attained. It is of interest to note that a relative 100% error in the determination of k for a hypothetical exchange model ($T = 300$ K, $k = 100$ s^{-1}), with an error of ±6 K in the determination of temperature, leads to a relative error in the estimate of $\Delta G^{\neq}$ at the level of only 4.5%.

The enthaly $\Delta H^{\neq}$ and entropy $\Delta S^{\neq}$ of activation are found as the coefficients of the linear relation between $\ln(k/T)$ and T^{-1} based on Eqn.(12). The use of the Arrhenius equation $k = A_0 \exp(-E_a/RT)$ is less preferable because the condition that the frequency factor A_0 and the activation energy E_a are independent of temperature holds less vigorously. Calculation of $\Delta G^{\neq}$ by the equation

$$\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq} \qquad (14)$$

is unjustified, because the advantage of accuracy, which is guaranteed by the direct calculation using Eqn.(13), is thereby lost.

The accuracy of the estimation of the constant k depends mainly on the extent to which the optimum experimental conditions can be fulfilled, because there are no fundamental difficulties in the mathematical treatment of the spectra. The constant k can be estimated in two ways: by the one-parameter procedure or by the ATLS method. In the one-parameter method simple analytical relations between the constant k and some spectroscopic parameter, which can be obtained in the simplest cases, are used. The methods involving these relations have been discussed in detail.[18,19,31,34,50] An exhaustive analysis of the limits of applicability of the approximate formulae and the errors in the determination of k has been carried out.[34,57] The principal difficulty consists in the fact that the use of approximate relations yields a number of experimental points which is inadequate for a statistical treatment and as a result gives rise to a large random error. The size of the deviations depends on how rigorously the conditions of the approximation hold and in certain cases can exceed the random errors to such an extent that the value of the activation data obtained becomes doubtful. These systematic errors, which are difficult to take into account and which lead to large negative values of the entropy factor $\Delta S^{\neq}$, are also largely responsible for the "anomalous" values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$.

It has been shown[58,59] by means of special comparative analysis of the temperature variations of the spectrum that under favourable conditions the relative error in the estimation of $\Delta H^{\neq}$ with the aid of approximate formulae is not less than 2–3 kJ mol^{-1}, while ATLS yields an error of the order of 0.6–0.8 kJ mol^{-1}. Under these conditions, the differences between the average values of $\Delta H^{\neq}$ reached 20% (the approximate methods yield unduly low $\Delta H^{\neq}$). The attempts to improve the approximate formulae,[60] including the procedure involving the subdivision of the kinetic range into five intervals instead of the usual three,[61] do not in essence alter the situation. The systematic error factor can be to some extent weakened when the experimental conditions permit the employment of the approximate formulae over the entire kinetic range.[62] The use of these formulae is at present justified only in the region of slow exchange and for the determination of k at the collapse temperature T_c from the ^{13}C NMR spectra, because in the simplest exchange systems, where the one-parameter method is applicable, the line form can be readily calculated on a minicomputer under laboratory conditions.

In the ATLS method the rate constant k is found either by a visual comparison of the calculated spectra and spectra observed at a certain temperature or by resorting to iterative procedures (the method of "digitalisation of the spectra").[63,64]

According to Sandstrom's data,[34] the relative error of the constant k estimated by the spectrum digitalisation method is 5%, i.e. is of the same order of magnitude as in the visual comparison method; in other words, the accuracy of the determination of k by both methods approaches the limit set by the experimental error. However, in the analysis of the exchange in complex spin systems the visual comparison method is sometimes preferable.[65,66] We may note that, when the number of experimental points is sufficient, the method of least squares yields a random error in the estimation of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ comparable to the limit of accuracy under the conditions of a precision experiment.

The optimum conditions of the DNMR experiment are well known.[15,34,46] The importance of conditions such as a slow pass, the absence of phase and amplitude distortions, the monitoring of the resolution over the entire temperature range, etc. is self-evident. Numerous procedures for the measurement of the temperature of the specimen with a high accuracy are known[34] (±0.2–±0.5 K), so that the important problem of the measurement of the specimen temperature can also be excluded from consideration. We may note that in standard DNMR experiments the temperature of the specimen is determined indirectly from the readings of the instruments in the circuit for the electronic stabilisation of the temperature of the heat exchanger stream. Since the temperature calibration is extremely sensitive to the [heat exchanger] flow rate in the region of low temperatures, the readings of the instruments at temperatures below 203 K are as a rule too low, which leads to considerable systematic errors in the determination of $\Delta H^{\neq}$. If an internal NMR thermometer cannot be used for some reason, it is necessary to measure the temperature directly before and after recording each spectrum. The size of the temperature range is undoubtedly important, but, since it is determined solely by the characteristics of the specimen itself, it is necessary to take into account only that the greatest accuracy is achieved for a uniform distribution of experimental points over the temperature range.[34]

The principal source of systematic errors, which is not always subjected to a realistic assessment, is the errors in the determination of the parameters of the spectrum of the exchange partners and the difficulties in the establishment of their temperature variations, which is particularly important in systems involving a complex exchange. This problem is closely intertwined with the general problem of the role of the medium in kinetic experiments and assumes exceptional importance in experiments starting "with the specimen" (mainly in low-temperature studies), because the substance determines both the kinetic range (and hence also the temperature range of the measurements) and the conditions in the medium (these problems have not been reflected in the review literature concerning the solvent effect in NMR spectroscopy[67,68]).

Special difficulties do not arise when it is possible to record a series of spectra in the regions of slow and rapid exchange, since in this case it is possible to obtain not only sufficiently accurate values of δ, J, and $^*T_2$ but also their temperature variations in an analytical form, which are then taken into account in the ATLS. In such cases it is possible to obtain a high accuracy in the determination of the activation parameters: ±0.4–0.08 kJ mol^{-1} for $\Delta H^{\neq}$ and ±0.5–1.0 e.u. for $\Delta S^{\neq}$ [65,66,69] Since it is as a rule difficult to take into account all the sources of systematic errors, it is more reasonable to quote the overall error, which is of the order of ±2 kJ mol^{-1} for $\Delta H^{\neq}$ and ±2.5 e.u. for $\Delta S^{\neq}$ according to the data of Allerhand et al. [57] We may note that it is frequently necessary to introduce the spectroscopic parameters to some extent arbitrarily and one has to postulate just as arbitrarily that their intrinsic (non-exchange) temperature dependence has been maintained over the entire range of the measurements.

The error can therefore prove to be even greater, for example in the solution of dynamic problems in the low-temperature region where experimenters are forced to employ mixtures of solvent which behave differently in different combinations and at a different temperature. [70] The medium effect may become more difficult to take into account when the molecule is non-polar overall but its individual fragments are highly polar. This situation has been observed using specific solvents such as acetone, dimethyl sulphoxide, benzene, and chloroform, which tend to form complexes, hydrogen bonds, etc. (cases where the solvent, for example, chloroform, induces the same reversible changes as the usual intramolecular exchange [71] are not considered here). Such characteristics of the behaviour are to a large extent responsible for the "apparent effects" of the solvent on the activation parameters. It is in fact precisely this factor and not the use of approximate formulae, as believed by Sergeev[15] and Sandstrom, [34] and the simplifcation of the spectrum, as claimed by Ionin et al., [8] that is responsible for the frequently quoted anomalous values of E_a in dimethylformamide and other amides. [34,52,59,72] Thus use of approximate formulae merely increases the error. [73,74]

From the standpoint of the correctness of the comparative analysis of the activation data obtained in different solvents, particularly for systems with intramolecular non-mutual exchange, the actual dependence of these data on the type of solvent and on the concentration of the test substance in solution is of special interest.

We shall now turn to the results of precision experiments designed to investigate the influence of the solvent on $\Delta H^{\neq}$. The enthalpy of activation for cyclohexane ring inversion is almost independent of the type of solvent (methylcyclohexane, CS_2, hexadeuterioacetone) [75] and varies within the limits ±4 kJ mol^{-1} for acetone (in CCl_4, CH_2Cl_2, and $CDCl_3$ as solvents). [76] In amides and related systems the solvent effects on the enthalpy of activation for rotation about the C–N bond are expressed by a quantity of the order of ±4 kJ mol^{-1}; [71,77–80] an appreciable concentration dependence has also not been observed.

For systems with non-mutual exchange, such reliable results are not available. However, one can use data for the influence of the type of solvent on the enthalpy of the conformational equilibrium ΔH_0. [70] For example, the energy difference between the rotational isomers of 1-chloro-2-fluoroethane changes by 1 kcal mol^{-1} on dissolution in cyclohexane, while the corresponding change for *trans*-1,2-dichlorocyclohexane is by 0.89 kcal mol^{-1} [the correction for the temperature dependence of the dielectric constant $\varepsilon(T)$ was not taken into account]. It has been shown [81] that, within the framework of the theory of reactive fields, the correction for the temperature dependence of $\varepsilon(T)$ may be neglected in estimating the influence of the solvent on the conformational equilibrium with the aid of NMR: in substituted 1,3,2-dioxaphosphorinanes ΔH_0 varies within the limits 3.5–1 kJ mol^{-1} in a series of solvents—acetonitrile, acetone, methylene chloride, and carbon tetrachloride. Thus the medium factor can be taken into account in the comparative analysis of $\Delta H^{\neq}$, provided that the differences ($\Delta\Delta$) between the different media exceed 4 kJ mol^{-1}. For the free energy of activation, this range of $\Delta\Delta$ values is ±0.3–0.4 kJ mol^{-1} and for $\Delta S^{\neq}$ the $\Delta\Delta$ vary from ±4 to ±5 e.u. The quantities $\pm\Delta\Delta$ lie within a comparison region which can be easily established by analysing the activation data obtained for the same compounds under similar experimental conditions and using similar methods for the interpretation of the spectra (for example, on the basis of the data for cyclohexane quoted above). The same range of $\pm\Delta\Delta$ values has been obtained for the activation parameters determined in standard kinetic NMR experiments.

The discussion of the questions related to the effect of the solvent on activation parameters is outside the framework of the present review. There are numerous publications devoted to this problem. [82–85] It is very likely that in the immediate future, when it will be possible to survey the results of kinetic studies in highly diluted solutions and in the gas phase, the approach to this problem and the existing ideas will undergo radical changes. We may note that the temperature variation of the chemical shifts for reference compounds (tetramethylsiloxane, hexamethyldisiloxane, and benzene) [86–88] does not affect significantly the accuracy of the estimation of the activation data.

The questions concerning the experimental error become particularly important in the study of complex exchange, because here the accuracy is much more significant than in a standard kinetic experiment: insufficiently correct determination of the limits of the probable values of the activation parameters can cause an incorrect treatment of the exchange situation or can lead to the formulation of erroneous ideas about the molecular dynamics of the chemical system investigated.

The intepretation of the activation parameters for chemical exchange is to some extent an independent field of study, but, since these parameters are determined mainly by DNMR, the questions concerning their interpretation are deal with in virtually every serious DNMR study.

Since most of the chemical exchange processes involving polyatomic molecules take place without the participation of the excited levels of the molecule, the transmission coefficient κ in Eqn.(13) is assumed to be 1 or 0.5. The contribution of tunnelling to κ is neglected. This contribution becomes effective for low barriers to interconversions for molecules with few and light atoms. [89]

The constant k is related to the difference between the zero-point energy vibrations in the transition and ground states E_0 by the expression

$$k = \varkappa \frac{k_b T Q^{\neq}}{\hbar Q} \exp(-E_0/RT) , \qquad (15)$$

where $Q^{\neq}$ and Q are the partition functions for the transition and ground states and the relation between E_0 and V (see Figure), which is found with the aid of quantum-chemical calculations of the potential energy surface, is defined by the formula

$$E_0 = V + \sum_i^{\text{trans}} h\nu_i/2 - \sum_j^{\text{gr}} h\nu_j/2 ,$$

where the summation is carried out over the vibrational degrees of freedom for the transition and ground states.

It is assumed that all the vibration frequencies ν_i and ν_j are approximately the same with the exception of the single frequency ν, corresponding to movement along the reaction coordination. The difference between E_0 and V is $6\bar{\nu}$ kJ mol^{-1} ($\bar{\nu}$ is the wavenumber in cm^{-1}) and must be taken into account in the most accurate calculation; when the process is described in terms of torsional vibrations, whose frequencies are much lower, the above difference can be neglected. It follows from Eqn.(15) that

$$\Delta H^{\neq} = E_0 + RT^2 \, \mathrm{d} \ln \frac{Q^{\neq}}{Q} / \mathrm{d}T \,, \tag{16}$$

$$\Delta G^{\neq} = E_0 - RT \ln \frac{Q^{\neq}}{Q} \,, \tag{17}$$

$$\Delta S^{\neq} = R \ln \frac{Q^{\neq}}{Q} + RT \frac{\mathrm{d}}{\mathrm{d}T} \left(\ln \frac{Q^{\neq}}{Q} \right) \,. \tag{18}$$

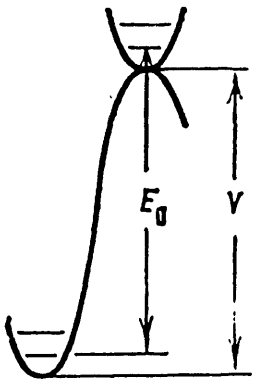


Diagram of the relative vibrational energy levels of the molecule: V = calculated theoretical energy; E_0 = zero-point vibration energy.

It has been suggested that the energy levels of the translational, rotational, and vibrational movements are mutually independent, i.e. $Q = Q_{\text{trans}} Q_{\text{rot}} Q_{\text{vibr}}$. For intramolecular exchange processes, evidently $Q_{\text{trans}} = Q_{\text{trans}}$ [sic].

(a) The activation enthalpy $\Delta H^{\neq}$. Since, as will be shown below, the ratio $Q^{\neq}_{\text{rot}}/Q_{\text{rot}}$ is independent of temperature, only the contribution of the vibrational partition functions Q_{vibr} must be taken into account in Eqn.(16). These partition functions differ only by the contribution q_r, which is determined by the degree of freedom of the vibrational movement at a frequency ν_r, which is absent in the transition state. Then

$$\frac{\mathrm{d}}{\mathrm{d}T} \left(\ln \frac{Q^{\neq}}{Q} \right) \simeq \frac{\mathrm{d}}{\mathrm{d}T} \ln \left(\frac{1}{q_r} \right) = \frac{\mathrm{d}}{\mathrm{d}T} \left\{ \ln \left[1 - \exp \left(- \frac{h\nu_r}{k_b T} \right) \right] \right\} \,,$$

whence

$$\Delta H^{\neq} = E_0 - R \frac{h\nu_r/k_b}{\exp (h\nu_r/k_b T) - 1} \,. \tag{19}$$

Thus $\Delta H^{\neq}$ depends on the temperature, but this dependence is not very pronounced and may be neglected. The difference $\Delta H^{\neq} - E_0$ approaches RT in the limit (at high values of T or at low frequencies ν_r) and can be calculated in principle.

The exceptional value of acurate experimental $\Delta H^{\neq}$ with correctly applied corrections is evident, since only by comparison with the latter is it possible to achieve a reasonable compromise in quantum-chemical calculations on the barriers. This applies both to *ab initio* calculations and to quantum-chemical calculations in terms of semiempirical approximations.[89-91]

The results of calculations have been discussed in the literature.[34,51] Strictly speaking, for comparison with such calculations, it is necessary to have the results of experiments in the gas phase, which, as will be shown below, lead to different values of $\Delta H^{\neq}$.

(b) The activation entropy $\Delta S^{\neq}$. This is a more "dynamic" activation parameter than $\Delta H^{\neq}$, but at the same time it is more difficult to use it for predicting the transition state. However, the view concerning this parameter has become optimistic in recent years. The initial scepticism was caused both by the large errors in the experimental estimates and by the problematic nature of the theoretical calculations of the entropy of the transition state. As a palliative measure, it was suggested that only the statistical contribution to $\Delta S^{\neq}$ be used on the basis of the symmetry properties of the molecule in the ground and transition states. This approach appears entirely convincing, because, subject to the assumptions underlying the estimation of the contribution of vibrational degrees of freedom to $\Delta H^{\neq}$, the contribution of the latter to $\Delta S^{\neq}$ is negligible[34] ($-0.20R - 0.03R$). Since the principal moments of inertia of the molecule I_A, I_B, and I_C in the ground and transition states can be assumed to be equal, it follows that the contribution

$$Q_{\text{rot}} = \frac{\pi^{1/2}}{\sigma} \left(\frac{8\pi k_b T}{h^2} \right) (I_A I_B I_C)^{1/2}$$

is determined only by the term $\sigma/\sigma^{\neq}$, where σ and $\sigma^{\neq}$ are the group orders of the pure rotations in the ground and transition states. Eqn.(18) can then be written in the form

$$\Delta S^{\neq} = R \ln \sigma/\sigma^{\neq} \,. \tag{20}$$

An additional term, namely the entropy of mixing $\Delta S^{\neq}_{\text{mix}}$, which takes into account the multiplicity of the degeneracy of the states, must be introduced into this equation:

$$\Delta S^{\neq}_{\text{mix}} = -R \sum_i P_i \ln P_i \,,$$

where P_i is the fraction of molecules passing through each transition state.

An alternative approach to the estimation of the statistical contribution to ΔS, consisting in the direct estimation of the number of independent ways in which the barrier can be crossed, is available. A discussion about these questions can be found in the literature.[34,92] However, analysis of a large amount of experimental data leads to the conclusion that this approach does not solve the general problem and furthermore is unjustified even in the simplest case—the description of the inversion of the ring in cyclohexane derivatives,[66] and it is essential to take into account all the contributions to $\Delta S^{\neq}$. However, although the difficulties expected in this procedure are evident, the conclusions reached by Hoffner et al.[66] give rise to a definite optimism. In certain cases it may be useful to discuss the problems in terms of the contributions to the partition functions by the rotational degrees of freedom of the internal rotors; however, this contribution is also insignificant.[34]

The above remarks concerning the corrections to $\Delta H^{\neq}$ and $\Delta S^{\neq}$ and the prospects for the employment of these quantities for the prediction of the transition state apply primarily to systems with the simplest form of the barrier profile under conditions where there are no medium effects. Here the

expected contributions to $\Delta S^{\neq}$ are small, of the order of magnitude of ±2 e.u., and comparable to the contribution of the statistical factor, while the accuracy of the experimental estimate can be raised to ±0.5 e.u. However, this problem has other aspects associated with the interpretation of the $\Delta S^{\neq}$ for a wide variety of compounds which are not merely of theoretical interest. These include the interpretation of the anomalously large positive and negative activation entropies, greatly exceeding their standard experimental error. Qualitatively, these effects have been explained as "entropy effects" of the highly polar interactions: they are caused by the considerable difference between the types of solvation of the molecules in the ground and transition states.[34,82] The sign of $\Delta S^{\neq}$ is determined by the relative polarity of these compounds: the large negative values correspond to molecules with a more polar form of the ground state (of the entire molecule or its individual fragments). It has been suggested that these effects can be used to predict the structure of the transition state.[83]

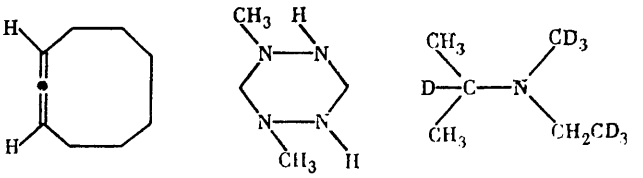
Another manifestation of the effects of this kind is large negative values of $\Delta S^{\neq}$ (up to −20– −30 e.u.), which are typical for tautomeric transformations in cyclic phosphoranes,[93] intramolecular phosphorotropic 1,3-migrations in a series of phosphorylated amidines,[94] and 1,3-sulphenyl migrations in amidine systems.[95] The negative entropies in the first two cases probably reflect the multistage mechanism of the processes described. Clearly, for such systems, theoretical calculations of the $\Delta S^{\neq}$ are hardly feasible in the immediate future. Nevertheless, the prospects for the employment of $\Delta S^{\neq}$ for the prediction of the transition state or at least for the explanation of the experimental results are entirely optimistic, particularly in the case where it is possible to develop reliable semiempirical rules in conjunction with the employment of a correct comparison of data for model compounds.

(c) The free energy of activation $\Delta G^{\neq}$. The high accuracy, the simplicity of the experimental estimation, and the principle of linearity[96,97] have been responsible for the employment of the most varied correlations of this parameter with the properties of the substituents, the medium, etc. in describing intramolecular exchange processes. Certain examples of such correlations have been given by Spaargaren et al.[58] However, we do not consider it necessary to discuss them within the framework of this review. We shall only mention the lack of validity of numerous discussions concerning the activation barriers ($\Delta H^{\neq}$) using free energy of activation data. Such identification is strictly speaking possible when the assumptions underlying the derivation of Eqns. (16)–(20) are valid. Furthermore, when the ATLS has not been carried out with a subsequent estimation of $\Delta H^{\neq}$ and $\Delta S^{\neq}$, the insensitivity of $\Delta G^{\neq}$ to errors in the determination of k and even to the values of k themselves can lead to an incorrect assessment of the exchange situation and hence to errors in the interpretation of different effects influencing the exchange processes. Evidently, in systems with a complex chemical exchange, the use of only the one parameter $\Delta G^{\neq}$ is impermissible.

3. Experimental Studies of Multiparameter Chemical Exchange

We shall consider more fully the studies by the ATLS DNMR method of systems in which a multiparameter exchange is observed and the constant k is determined from the temperature evolution of one group of lines in the spectrum.

In those cases where the processes are separated by a wide temperature range, it is in most cases possible to achieve a separate description of these processes, for example, in terms of the changes in the ^{13}C NMR spectra of cyclonona-1,2-diene (I) in the temperature range 96–263 K.[98]



(I) (II) (III)

The resonance line of the carbon atom in the C–H group, which is a singlet at room temperature, splits into two lines at 123 K with an integral intensity ratio of 2 : 1, of which one, the low-field line, is greatly broadened; on further decrease of temperature, it divides into two lines of equal intensity (at 103 K). These spectral changes correspond to two intramolecular processes: (a) the pseudorotation of the dominant (asymmetric) conformation, which averages out two non-equivalent signals; (b) the interconversion of the type "dominant" form ⇌ minor "symmetrical" conformation, which is responsible for the merging of all the signals into a singlet. Anet and Yavari[98] were able to determine the kinetic parameters of these processes with adequate accuracy.

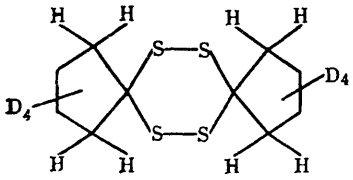
The rates of intramolecular topomerisation have been determined with the aid of the ATLS of the signal of the methylene protons in the ^1H NMR spectra of 1,4-dimethylhexahydro-1,2,4,5-tetrazine (II):[99] the rates of ring inversion and of the inversion of the bond pyramid at the nitrogen atom. Here the changes in the spectrum of the CH_2NH fragment in the temperature range 233–273 K are entirely due to the change in the rate of inversion of the nitrogen atom associated with the intermolecular hydrogen exchange involving the NH groups: the rate constants k were obtained on the assumption that the rate of ring topomerisation is low and does not influence the observed line form. The temperature range of the observed changes in the spectrum as a consequence of the topomerisation of the ring was 253–310 K.

Two intramolecular processes in deuteriated *N*-ethyl-*N*-methylisopropylamine (III) have been investigated:[100] (a) the inversion of the bond pyramid at the nitrogen atom, which is manifested by the exchange broadening of the ^1H NMR signals in the temperature range ~133–152 K, and (b) the rotation about the C–N bond, which contributes to the change in the ^1H NMR line form at 101–124 K. The kinetic parameters of both processes have been estimated on the assumption that the rotation takes place under the conditions of hindered inversion.

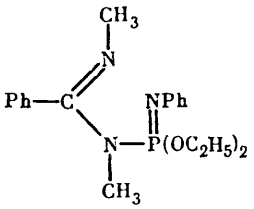
In this case, when the exchange processes responsible for the broadening of the NMR lines are separated by a short temperature range (20–30 K), the task of finding the kinetic parameters may be greatly complicated as a consequence of the uncertainty, noted above, in the determination of the constant k not only in the region of fast exchange but also in the region of slow exchange. If the signals of the "frozen out" forms are characteristic and fairly well separated in terms of the chemical shift scale, then in some cases, for example, when the region of the slow exchange covers a wide temperature range, it is possible to determine the kinetic and activation parameters for exchange processes on the basis of the ATLS of the low-temperature NMR spectrum.

The temperature dependence of the ^1H NMR spectrum of 3,3,6,6-bis(tetradeuteriotetramethylene)-*S*-tetrathiane (IV) has been described in this way[101] within the framework of the chair–twist–chair*–twist*# equilibrium, because the temperature range corresponding to the slow (in terms of the NMR scale) exchange is ~50 K:

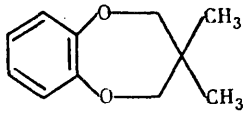
The asterisk denotes inverted structures.



(IV)



(V)

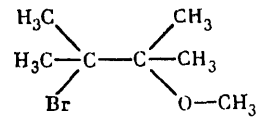


(VI)

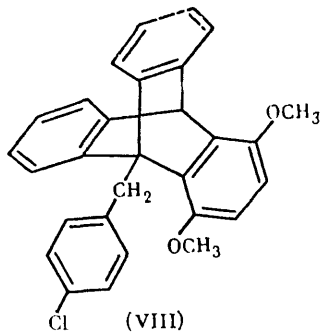
The authors showed that the introduction of a rate constant for the direct chair ⇌ chair* or twist ⇌ twist* transitions leads to a deviation of the calculated line form from the experimental form, whence it followed that the energy barriers in these transitions should indeed be higher than for the chair ⇌ twist exchange.

The kinetics of *Z*–*E* isomerisation and phosphorotropic tautomeric processes have been investigated on the same lines[94] for N^1N^2-diethoxy-N^1N^2-dimethyl-*N*-phenyliminophosphonylbenzamidine (V) (in this case the line form is calculated mainly in the region of slow exchange at 418–445 K). In those instances where the NMR spectra of the "frozen out" forms are only slightly separated in terms of the chemical shift scale, the uncertainty in the determination of the constant *k* may prove to be significant over the entire temperature range of the spectroscopic changes and can lead to errors in the determination of the activation parameters. Thus, in a study[102] of 3,3-dimethyl-1,5-benzodioxepan (VI) the ^{1}H NMR spectra of the "frozen out" chair and twist forms were observed at 133 K. The rate constants for the chair–chair and chair–twist transitions in the inversion of compound (VI) were determined by the ATLS method, but the authors[102] do not consider it possible to discuss the energy relations of the processes on the ground of the unreliability of the determination of temperature, the inaccuracy in the determination of the quantities $1/^*T_2$, and also the use over the entire temperature range of postulated relative proportions of the conformers; in the authors view, the anomalously large negative $\Delta S^{\neq}$ (−15 ± 5 e.u.) are a consequence of these errors. We believe that this is caused to a large extent by the erroneous nature of the estimation of the kinetic parameters of the exchange as a result of the uncertainty in the derivation of these parameters, because the changes in the spectrum corresponding to the above processes are manifested in virtually the same temperature range and the authors[102] do not quote alternative calculations of the rate constant which are essential in such cases.

A ^{1}H NMR study of the hindered rotation about the C–C bond in a series of 2-alkoxy-3-halogeno-2,3-dimethylbutenes has been reported.[103] The singlet due to the methyl groups (CH_3^*), observed in the spectrum of compound (VII)



(VII)



(VIII)

at room temperature splits into three lines at 162.5 K: an intense singlet and two lines with equal integral intensities, the ratio of the integral intensity of the first line to the sum of the other two being 43 : 57. This change in the signal of the methyl groups is caused by the decrease of the rate of rotation about the C–C bond when the rotational process can be regarded as exchange between the *trans*- and *gauche*-forms (a) and between two *gauche*-forms (b). Using the ATLS, the authors point out that it is impossible to differentiate the temperature dependence of the rate of the second process, because the theoretical line forms obtained with and without allowance for k_b do not reveal a significant difference (the spectra for $k_b = 0$ and $k_a = k_b$ were calculated) and are close to the observed line forms.

A study[104] of the hindered rotation about the C–C bond in 9-(*p*-chlorobenzyl)-1,4-dimethoxytriptycene (VIII) is instructive in this connection. At a low temperature (~246 K) the ^{1}H NMR signals of the methylene protons consist of an AB quartet and a singlet, due to the *d*-, *l*-, and *meso*-forms respectively. An increase of temperature leads to the merging of these signals into a singlet. It has been shown that, for different selections of the rate constant k_1 and k_2 for the *meso* ⇌ *d*(*l*) and *d* ⇌ *l* exchange processes respectively, the calculated line form agrees with the observed line form and the ranges of the constants k_1 or k_2 in which this occurs are comparable to the true values of k_1 or k_2. The authors[104] formulated the problem of the estimation of the kinetic parameters of exchange processes having similar rates and responsible for the exchange-induced broadening of a single group of NMR lines, but do not propose a solution. The solution of a similar problem for mutually independent processes has been described.[105] The uncertainty in the estimates of k_1 and k_2 (for two independent processes) can be expressed graphically by a family of $\ln k_1 - \ln k_2$ "iso-F" curves, along which the theoretical line form agrees with the experimental line form at a specific temperature when different sets of k_1 and k_2 are used. In order to find the solution, a series of straight lines intersecting the "iso-F" curves are drawn and the points of intersection are transferred to $\ln k_1 - T^{-1}$ and $\ln k_2 - T^1$ plots. A unique solution, corresponding to a real process, is found from the minimum standard deviation of the linear relations found in this way between $\ln k_1$ and $\ln k_2$ and temperature.

The examples examined are distinguished by the simplicity of the exchange situation, because the exchange mechanism is known. However, there are many systems in which there is a possibility of different versions of the exchange process and the choice of an unambiguous solution is an extremely complex problem, which probable cannot always be solved by the ATLS DNMR method. It can be solved fairly rigorously for the simplest case where the intramolecular exchange is characterised by a single rate constant and it remains only to find an alternative exchange mechanism. This problem has

been discussed in detail in a review,[30] where it is shown that in such cases agreement between the calculated and experimental line forms over the entire temperature range is a criterion of the reliability of the selected model. However, it is not always possible to predict the ways in which the exchange mechanisms can increase in complexity or to describe quantitatively this kind of chemical exchange in cases where an increase in its complexity has been established experimentally.

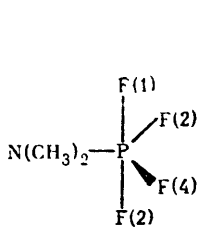
On the basis of the analysis of numerous experimental data and our own studies, we propose three criteria for the reliability of the description of complex chemical exchange, whose employment makes it possible to avoid errors in the interpretation of DNMR data:[106]

1. agreement between the calculated and observed NMR line forms over the entire temperature range;
2. the linearity of the temperature variation of the rate constants for the processes;
3. agreement between the activation parameters obtained as a result of the analysis of multiparameter exchange with the analogous values for systems where the particular process is unique.

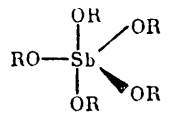
Examples which logically reflect the application of these criteria with increasing complexity of the exchange situation are presented below. One of the first studies of this kind was that of Saunders (see Steigel[30]), who investigated the degenerate shift of the methyl group in the heptamethylbenzenium ion. Two possible versions of the exchange were considered: in one case the methyl group passes to a neighbouring position (the 1,2-shift), whereas in the other the shift is random. Depending on the pathway followed in the shift, two versions of the transitional structure are also possible. Analysis of the ^{1}H NMR line form made it possible to give preference to the first exchange mechanism. The problem of the intramolecular exchange of the $CuP(C_2H_5)_3$ group in the $C_5H_5CuP(C_2H_5)_3$ molecule, in which the group either shifts to a neighbouring position or there is exchange between the 1- and 3-positions, has been solved analogously.[30,107] The calculated line forms for these exchange mechanisms differ appreciably; comparison with experiment has shown that the exchange proceeds via the 1,2-shift mechanism.

Processes leading to the averaging of the ^{1}H NMR spectra of *O*-acyl-3,7-dibenzyltropolones have been identified.[108] The ATLS method enabled the authors[108] to identify, together with the acyltropic tautomerism, two conformational transitions, namely the rotation of the acyloxy-group about the troponyl–O bond and the rotation of the acyl group in the acyloxy-fragment.

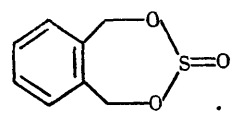
In the study of intramolecular dynamic processes in the phosphorane $PF_4N(CH_3)_2$ (IX),[30,109] it proved possible to distinguish two mechanisms of the rearrangement: the one-pair and two-pair ligand exchange processes in the pseudorotation of the bonds, i.e. the 1–4, 1–3, 2–3, and 2–4 or (1–3)(2–4) and (1–4)(2–3) ligand exchange processes. Analysis of the ^{31}P NMR line form permitted the unambiguous selection of the second type of rearrangement:



(IX)



(X): a) $R = CH_3$; b) $R = CH(CH_3)_2$

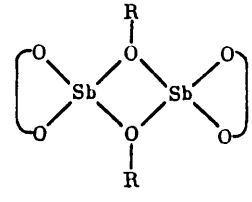


(XI)

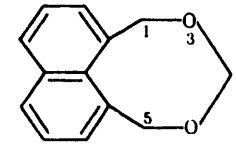
The possible mechanisms of the exchange in the dimeric structure of pentamethoxyantimony (Xa) have been examined.[110] It has been established that the mechanism according to which there is exchange between the dimeric structures (dissociation and formation of bridge bonds) operates and that, simultaneously with the rupture of the bridge bonds, the configuration of the bonds at the Sb atom changes, both processes being characterised by different rate constants.

The determination of the components of the conformational equilibrium using DNMR can be illustrated in relation to the analysis of the line form in the spectrum of the methylene protons of phthalyl sulphite (XI). The form of the low-temperature spectra indicates the appearance in solution of two forms[111,112] (two AB quartets). The "chair-a" conformation (with the axial position of the S=O bond) predominates. Additional arguments in favour of the second, "twist" conformation were obtained on the basis of the ATLS, because the exchange mechanism in which the low-field and high-field lines of the two AB quartets are averaged out corresponds to the real process. If the alternative "chair-e" conformation were realised, the mechanism would have corresponded to the averaging out of the high-field signal of the dominant form with the low-field form and conversely.

The use of the ATLS made it possible to establish for the first time that, as a result of the dynamic processes manifested in the ^{1}H NMR spectra, in the cyclic compounds of tricoordinate antimony the bond pyramid undergoes a change in its configuration.[113,114] It has been established that the monomeric form in the "chair-a" conformation and the dimeric form (XII) exist in solution and that exchange between them in fact reflects the evolution of the line form in the NMR spectra.



(XII)



(XIII)

In the examples quoted the first of the proposed criteria for the description of intramolecular chemical exchange processes in terms of DNMR was applied. Fundamental information about the validity of the description can be extracted from the analysis of the temperature dependence of the rate constant for the process described. When a suitable mathematical model of the real exchange mechanism is used, this dependence should be linear in terms of a plot of $\ln(k/T)$ against $1/T$ and, since changes in line form are observed over a narrow temperature range (~50 K), it should also be linear in terms of a plot of $\ln k$ against $1/T$. This approach is based on the high accuracy of the estimation of the activation parameters reached in the ATLS method.

A study of the molecular dynamics of 2,4-dioxa-3,5-dihydro-1*H*-cyclo-octa[*de*]naphthalene (XIII) showed[115] that calculation of the ^{1}H NMR line form for the methylene groups in the 1(5)- and 3-positions on the assumption of mutual conformational exchange led to its agreement with the experimental line form over the entire temperature range for both groups of protons. However, the differences between the values of k at the same temperature for the above groups of protons greatly exceeded the experimental error and the dependence of $\ln k$ on $1/T$ could not be fitted by a straight line. Analysis of the variation of the non-equivalence of the chemical shifts of the methylene protons at C(1) [C(5)]

in 3-*t*-butyl-2,4-dioxa-3,5-dihydro-1*H*-cyclo-octa[*de*]naphthalene (XIV) made it possible to establish that the change in the line form for compound (XIII) is caused by the chair–chair exchange in the presence of rapid chair–boat exchange. Calculation of the line form corresponding to this exchange mechanism, using the spectroscopic parameters of the "chair" and "boat" forms of compound (XIV) yielded a satisfactory linear temperature variation of the rate of the chair–chair transition for compound (XIII).

This principle was also used in the solution of the previously discussed problem of the separation of the contributions of the exchange processes occurring at similar rates and responsible for the exchange-induced broadening of one group of NMR lines.[105]

Using the same procedures, the "synchronous" nature of the rotation of a pair of rings in the collective internal rotation of the three aromatic rings in the triaryl derivatives of arsenic and phosphorus has been demonstrated[116] on the basis of the ATLS of the ^{19}F DNMR spectrum.

Finally there is a possibility of the situation where the changes in the NMR spectra are caused by processes whose spectroscopic assignment gives rise to no doubts and the $\ln(k/T)-1/T$ relation is linear. In this case it is necessary to employ a third criterion.

Thus, in the study quoted above,[99] identical activation energies were obtained for both processes and, on the basis of a comparison of this quantity with the literature data for similar processes, the authors concluded that their rates are limited by the inversion of the bond pyramid at the nitrogen atom. Olekhnovich et al.,[108] who noted the auxiliary role of the conformational transformations in acylotropic tautomerism, were guided by the same principle.

In the study quoted above,[110] approximately equal values of $\Delta H^{\neq}$ were obtained for the exchange of the dimer–dimer type involving compound (Xa) and for the pseudorotation of its bonds (~76 kJ mol^{-1}); the latter cannot be accounted for in terms of the ideas concerning the energy relations of the pseudorotation of the bonds of the pentacoordinate P, As, and Sb atoms, although the spectral changes in the case under consideration are consistent with the pseudorotation process. The study of the NMR for the monomeric compound (Xb) showed[110] that the barrier to the pseudorotation of the Sb^{V} bonds does not exceed 20 kJ mol^{-1}. The activation parameters for compound (Xa) were interpreted within the framework of ideas concerning the rate-limiting stages in the processes.

By virtue of the improvement in the computational procedures and in the apparatus, one can probably expect in the immediate years ahead a considerable progress in the study of systems with complex chemical exchange.

III. SPECIAL METHODS

1. The ATLS of Nuclei Other than ^1H

The exchange-induced broadening effects in the resonance absorption spectra of various nuclei with a spin of 1/2 (^{19}F, ^{13}C, ^{31}P, and ^{15}N) are described by the same equations as in the ^1H spectroscopy (the presence of a quadrupole moment in nuclei with a spin greater than 1/2 and their greater spin multiplicity make relaxation methods preferable to ATLS). The ^{19}F and ^1H NMR spectroscopic methods have similar sensitivities and the methods of the kinetic investigations using these nuclei differ little. The employment of the ATLS of the NMR spectra of the remaining nuclei has many features in common, which involve the sensitivity and the time scale of the method as well as the procedure used to record the spectra, which, considered together, distinguish the DNMR spectroscopy involving these nuclei from ^1H DNMR.

In the course of its rapid development, ^{13}C DNMR spectroscopy has already passed the inevitable period involving comparison with the scope of ^1H DNMR. Its advantages and, equally, its limitations and experimental difficulties have been demonstrated in relation to extensive experimental data,[27,29,34,117–119] which cannot be discussed within the framework of this review. We shall only touch upon some of the most important methodological aspects.

It is known that the range of the ^{13}C chemical shift (in p.p.m.) is ~20 times greater than that of the ^1H NMR shifts (or ~5 times greater in terms of frequency units). The range of the measurable rate constants therefore increases by a factor of 25 towards higher rates and collapse is reached at higher temperatures. However, one should note that, within the limits of a single structural fragment, an increase in the shift scale may not in fact occur.[113,120] In other cases the difference between the ^{13}C chemical shifts for the exchanging positions is so great that the advantage of a more extended time scale is transformed into a disadvantage of the method;[121] the region of the collapse and of the intermediate exchange occupies such a wide spectral range that the broadened spectral line merges with the base line. For "moderate" barriers (~40–60 kJ mol^{-1}), this region covers a wide temperature range and none of the regions of the rapid or slow exchange can be reached, which can lead to an erroneous interpretation of the spectrum.

In dynamic ^{13}C NMR with broad-band ^1H decoupling the exchange situation is relatively simple—it involves as a rule a two-sided exchange in a system of uncoupled spins, which has in fact led to numerous kinetic studies using ^{13}C NMR spectroscopy. However, serious experimental problems have been encountered, which must be taken into account in selecting the research methods. In the main they are associated with the low sensitivity of ^{13}C NMR spectroscopy and relaxation processes.

Special difficulties do not arise in studies with liquid specimens or with highly concentrated solutions. Here it is comparatively simple to attain a satisfactory signal-to-noise ratio in the region of the intermediate exchange in order to be able to employ the ATLS (naturally for moderate degrees of nonequivalence of the chemical shifts, amounting to ~200 Hz). However, it is usually necessary to work with dilute solutions, which requires a large number of accumulations. The time taken to record a single spectrum is so prolonged that the recording of a high quality spectrum in the region of intermediate exchange rates and collapse becomes extremely problematical, since it becomes essential to ensure a long-term stability of temperature and of its measurement.

This time factor becomes especially important in low-temperature measurements in solutions of sparingly soluble crystalline substances: after prolonged exposure to low temperatures, the substance crystallises. The measurement of temperature in the ^{13}C NMR method becomes very important in the recording of spectra with broad-band suppression of the ^1H signal, because the interaction of the microwave frequency radiation with a polar solvent leads to additional heating of the specimen (the degree of heating is proportional to the polarity of the solvent). For this reason, in those cases where a quantitative treatment of the temperature dependence of the ^{13}C NMR spectra is necessary, it is desirable to employ a ^{13}C NMR thermometer. The use of wide bulbs in order to increase the sensitivity creates certain difficulties in the measurement of temperature as a consequence of the high temperature gradient in the specimen (2 K cm^{-1}).

The relaxation processes are directly reflected in the accuracy of the determination of k from the exchange-induced broadening of the spectra. The point is that even in a single

exchange pair the relaxation times T_1 and the nuclear Overhauser effect (NOE) differ. This is clearly manifested in the region of a slow exchange, where the integral line intensities are inconsistent with the number of exchanging spins. An accurate analysis of the line form presupposes the knowledge of the temperature variation of T_1, which is not feasible owing to the chemical exchange effects.

Since the line width in the ^{13}C NMR spectra is just as small as in the ^{1}H NMR spectra, in kinetic studies it is very important to ensure the highest possible resolution determined by the capacity of the minicomputer. Such resolution is specified by the condition[34,122] $\Delta\nu = 2w/N$, where w is the width of the spectrum in the given frequency range and N the number of selected points on the descending component of the induction signal(DIS) (their uniform distribution on the DIS curve is assumed), i.e. $\Delta\nu$ is the distance between two points in the frequency range. Consequently the uncertainty in the determination of the line width is $2\Delta\nu$. Since the number N is limited by the capacity of the minicomputer, an improvement of the potential resolution is achieved by reducing w (in order to avoid the convolution of the spectrum, it is necessary to adjust the frequency range). For example, a resolution of 1.2 Hz is attained in the presence of 8192 points on the DIS curve for a width of the spectrum of 5000 Hz.[27] Since the error in the determination of the width of the exchange and non-exchange lines is ±1.2 Hz, for an exchange-induced broadening less than 10 Hz the constants k will be found with large errors. Another limiting factor and source of errors is the line broadening as a consequence of the residual splitting arising as the power of the microwave frequency field of the broad-band decoupling diminishes (the power is reduced in order to diminish the heating of the specimen).

It is easily seen that the ATLS method appplied to ^{13}C DNMR encounters serious difficulties and is justified only in those cases where the exchange problem cannot be solved by ^{1}H DNMR either due to the complexity of the spectra (for example, in the case of exchange in a five-spin or even more complex systems) or because the chemical exchange process itself cannot be observed.

We shall not dwell on well-known examples illustrating the inapplicability of ^{13}C DNMR spectroscopy to the study of certain types of chemical exchange, which can readily be identified by ^{1}H DNMR methods. We shall merely draw attention to the fact that the combined employment of both methods can be exceptionally useful in the analysis of systems with complex chemical exchange. The point is that in ^{13}C NMR spectroscopy one observes fairly frequently several exchange pairs simultaneously and the exchange processes can be manifested in different pairs. On the other hand, the same process can be reflected in different ways in the ^{1}H and ^{13}C NMR spectra, which makes it possible to avoid the uncertainty discussed previously. This approach has been illustrated by Sandstrom and Sjostrand.[123]

The ^{15}N NMR time scale is of the same order of magnitude (in terms of frequency units) as the ^{13}C NMR spectroscopic scale, but the sensitivity of ^{15}N spectroscopy is lower by two orders of magnitude than that of ^{13}C NMR. Kinetic studies on specimens with the natural abundance of the ^{15}N isotope therefore involve even greater difficulties. There has been only one investigation[124] of the hindered rotation about the C–N bond in L-arginine using ATLS. There have been more investigations using relaxation methods.[125] A number of studies have been carried out with the aid of the ATLS of the ^{15}N NMR spectra of enriched specimens, but these studies have been mainly devoted to intramolecular and intermolecular hydrogen exchange processes.[126–130].

The ^{31}P NMR time scale in frequency units is somewhat narrower than in carbon spectroscopy (by a factor of ~1.5), but, since the sensitivity of the ^{31}P NMR method is somewhat lower than that of ^{1}H NMR (by a factor of ~20), the difficulties are associated mainly with the relaxation processes when broad-band $^{31}P-\{^{1}H\}$ decoupling is used. There have been few studies carried out using ATLS. The intramolecular rearrangements in which the chemical shift of the signal due to the phosphorus nucleus remains unchanged but the line form is altered by virtue of the transposition of the spins linked to the ^{31}P nucleus are perhaps of greatest methodological interest.[109] Kinetic experiments under the conditions of selective $^{31}P-\{^{1}H\}$ decoupling will probably yield much information.

2. Kinetic Studies under Extreme Conditions. Gases. Liquids at High Pressures

Theoretical calculations of the activation and equilibrium parameters of chemical exchange are usually carried out for isolated molecules and until recently the calculated data have been compared with the results of studies in solutions. However, even the early ^{1}H DNMR data for the gas phase showed how incorrect is such a comparison.[131,132] There is no doubt that these experiments cannot be performed for every substance, but the exceptional value of experimental data of this kind has stimulated studies on these lines and their number has appreciably increased in recent years.

The main requirements which must be met by the given substance is a fairly high barrier to intramolecular transformations and volatility. A low concentration of the test substance is a very serious but not insurmountable obstacle in the experiments. Another cause of the reduced sensitivity is the broadening of the lines in the spectra for the gas phase owing to the low times T_1, because the mechanism of the spin–rotational relaxation in gases is more effective than in liquids.

The experimental technique has already been discussed.[132, 136] The Table presents the results of kinetic studies for the ATLS of the ^{1}H DNMR spectra for classical types of chemical exchange. On the basis of the very few data available, one can merely make general remarks. The temperature of the collapse with transition to the gas phase as well as the values of $\Delta H^{\neq}$ and k for different compounds vary in different ways. The times T_2 depend markedly on the pressure (the temperature and pressure dependences of the static parameters δ and J had been determined earlier and have been the subject of other investigations—see, for example, Raynes and Chadburn[138] and Bernstein[139]).

Interesting data have been obtained for the phase dependence of the rate constant and activation parameters for ring inversion in cyclohexane.[135,136] Assuming that the internal pressures in gaseous and liquid CS_2 at 298 K are respectively 0 and 3714 atm, while the difference between the values of $\Delta G^{\neq}$ in the gas phase and in the CS_2 solution is 370 cal mol^{-1}, then the activation volume is $\Delta V^{\neq} = -4$ cm^3 mol^{-1} [$\Delta V^{\neq} = (\partial G^{\neq}/\partial p)_T$]. This result is correlated with data obtained recently in the kinetic studies on cyclohexane ring inversion in various solvents at a variable pressure.[74] When the pressure is varied from 1 to 5000 atm, the $\Delta V^{\neq}$ vary from −5.0 cm^3 mol^{-1} (in acetone) to −1.5 cm^3 mol^{-1} (in $C_6D_{11}CD_3$), which is also consistent with the results of a study in which data for *NN*-dimethylacetamide were discussed.[140]

These experiments showed that, in the absence of strong electrostatic interactions, the activation parameters depend greatly on the state of aggregation. Few studies of this kind have been made. Experiments at a high pressure using shift reagents have been reported.[141] Data obtained in NMR studies of the influence of pressure on chemical kinetics[142] and molecular conformations[143,144] are available. The experimental technique is specific and has been discussed in the original communications.

Activation data for chemical exchange in liquid and gas phases.

Compound	Type of process	Conditions	T_c, K	$\Delta G^{\neq}$, kJ mol^{-1}	$\Delta H^{\neq}$, kJ mol^{-1}	$\Delta S^{\neq}$, e.u.	Refs.
NN-Dimethylnitrosamine	hindered rotation	pure liquid	456	97.4	—	—	[34, 131]
NN-Dimethylnitrosamine	hindered rotation	gas	431	88.4	—	—	[34, 131]
Aziridine	inversion of nitrogen	in CCl_4	298	72.7	76.1±2.0	−6.2±1.4	[132]
Aziridine	inversion of nitrogen	in decalin	298	71.5±3.0	63.9±1.6	+2.7±2.0	[132]
Aziridine	inversion of nitrogen	gas	338	72.0±0.2	63.5±2.6	−6.2±1.3	[132]
NN-Dimethylthioformamide	hindered rotation	pure liquid	473	106.6	—	—	[34, 133]
NN-Dimethylthioformamide	hindered rotation	gas	420	94.1	—	—	[34, 133]
NN-Dimethylacetamide	hindered rotation	in CCl_4	298	72.3	—	—	[77]
NN-Dimethylacetamide	hindered rotation	gas	305	65.5±0.4	—	—	[134]
NN-Dimethyltrifluoro-acetamide	hindered rotation	10% in CCl_4	—	74.4±1.6*	73.6±2.5	−0.6±2.0	[137]
NN-Dimethyltrifluoro-acetamide	hindered rotation	gas	—	68.5±2.0	67.3±2.0	−1.1±0.3	[137]
Cyclohexane	ring inversion	10% in CS_2	—	42.6	45.1	+2.8	[135, 136]
Cyclohexane	ring inversion	1% in CS_2	—	42.2	43.0	+0.6	[135, 136]
Cyclohexane	ring inversion	gas (333 kPa)	—	43.4	50.4	+5.7	[135, 136]

*Here and below in the Table the determinations were made at 298 K.

3. Special Methods

Fairly numerous methods, supplementing or modifying the classical ATLS method, are known. Many of these have been used since the beginning of intensive investigations of DNMR and are well known. They include the isotope tracer method,[15,34,145] the employment of lanthanide shift reagents,[34,146,147] and the direct stereomutation method (the equilibration method) proposed by Mannschreck[148] and developed in subsequent studies[149,150] (for a discussion, see Sergeev[15] and Sandstrom[34]). Studies of the internal movements of molecules dissolved in nematic media are of special interest. They are based on the high sensitivity of the spectra of partly oriented molecules to chemical exchange processes, which average out certain direct dipole–dipole interaction constants. Their energy barriers can be estimated quantitatively, provided that the intramolecular movement and the rotation of the molecules as a whole in the liquid crystal mesophase matrix are independent. The method involves also other assumptions and limitations, but it is nevertheless extremely attractive because it makes it possible to obtain activation parameters which cannot be determined by other procedures (low barriers, barriers in systems where there are no suitable NMR labels for investigation by standard methods).

A detailed discussion of this method, which is in essence a component of NMR investigations in the mesophase, may be found in the article of Emsley and Lindon.[151] We may note certain publications in recent years devoted to the study of ring inversion in S-trioxan,[152] the pseudorotation in cyclopentane,[153] and internal rotation in alkylamides in a polystyrene matrix.[154]

When spectrometers operating at markedly different frequencies ν_0 are available, it appears very attractive to make use of the simplicity and relatively high accuracy of the determination of k at T_c from a relation of the type $k = \pi\Delta\nu/2^{1/2}$ for mutual exchange, where $\Delta\nu$ is the limiting line separation. Since $\Delta\nu$ depends on ν_0, it follows that T_c also depends on ν_0 (in amides T_c changes by 3 K when the frequency is altered from 60 to 220 MHz). This method is believed[155] to guarantee a high accuracy of the estimation of $\Delta H^{\neq}$ and $\Delta S^{\neq}$. In individual instances this is probably valid, but one should note that the accuracy of the recording of collapse is low and is in fact lower the greater the rigour with which the condition governing the applicability of this formula is fulfilled. The collapse temperature T_c is determined to within 2 K and the presence of 3–4 points over a narrow range cannot ensure a high accuracy of the interpretation of an equation of type (12). However, the main deficiency of the method is the unjustifiably large consumption of apparatus time: in essence, it is necessary to carry out the entire kinetic experiment, from slow exchange to collapse, on several spectrometers, because, the occurrence of collapse must be determined very accurately. There is no doubt that in many cases it is essential to use the same NMR thermometer.

Major difficulties arise in the use of formulae for mutual exchange which relate k in the vicinity of collapse to the spectroscopic parameters and which include the working frequency ν_0 as the variable parameter.[156] The above methods have not found extensive application probably for this very reason. The use of the effect of the "concertina chemical shifts", arising when a train of four pulses with phase rotation by 90° is employed, appears more attractive.[122] In media of low viscosity, where there is no dipole–dipole broadening, the duration of the pulses can be regulated in such a way that the chemical shift scale varies from 0 to 1, while the indirect spin–spine coupling constants remain unaltered. This technique, which has become available in recent years, can prove extremely useful in the analysis of exchange in complex spin systems and in systems with multiparameter exchange (and naturally when the above methods with variation of ν_0 are employed).

The method involving a rapid change of the medium[157] has been proposed for the investigation of hindered rotation in molecules which cannot be heated owing to their thermal instability. It is applicable in the presence of fairly high energy barriers when the equilibrium depends markedly on the solvent polarity and the equilibration time is long enough to record the NMR spectra. The experimental technique is fairly simple: the test substance is rapidly mixed with the solvent with a markedly different polarity and the attainment of a new equilibrium at a certain temperature is then observed. The scope of the method has been illustrated in relation to the study of the hindered rotation about the C–C bond in 9-(2-methoxy-1-naphthyl)-9-fluorol.

A high accuracy of the estimation of $\Delta H^{\neq}$, to within 3 kJ mol^{-1}, was attained. The limitations of the method are self-evident: the usual problems involving the employment of mixed solvents and the inconsistency of the observed heights of the barriers with the quantities obtained in non-polar solvents remain. It is easily seen that the method is similar to the direct stereomutation method already mentioned.

4. Relaxation Methods

Standard selective relaxation methods make it possible to obtain the same information about chemical exchange processes as DNMR is a stationary regime, but their application in the region of intermediate rates of exchange is less preferable, mainly due to the high errors in the determination of the rate constant k. In the regions of slow and rapid exchange, which are limiting as regards the ATLS, the relaxation methods yield more accurate values of k.

Methods involving the use of relaxation processes, which can yield data inaccessible by the ATLS method, are known. One of these involves the measurement of the relaxation time T_1 in a rotating coordinate system.[34,158] The nuclear spin system is acted upon by a 90° microwave pulse with an amplitude B_1 along the x axis. At the instant when the precessing (with a frequency $\nu_1 = \gamma B_1/2\pi$) vector with a magnetisation M is aligned rigorously along the y axis, the phase of the pulse is altered by 90° and it is applied along the y axis. Since the vectors B_1 and M are now parallel, the vector M is maintained along the y axis. This entails an exponential decrease of the length of the vector M with a characteristic time T_1. In the simplest case of a two-sided exchange we have

$$(T_{1\rho}^{-1})_{exch} = T_{1\rho}^{-1} - T_1^{-1} = \frac{\pi^2 k \cdot \Delta\nu^2}{k^2 + 4\pi^2 \nu_1^2} .$$

This relation is valid subject to the conditions $\Delta\nu^2/k \ll 1$ and $\Delta\nu \ll \nu_1 \ll \nu_0$. The method makes it possible to measure rates in the range 10^3–10^6 s^{-1} and to determine $\Delta\nu$, which is impossible in direct experiments in this range of rates.

In another method, proposed by Hoffman and Forsen[24] and known as the "saturation transfer method", the direct NOE is used in systems with slow chemical exchange. A procedure based on the cross-relaxation NOE has also been developed.[160,161] The idea of the saturation transfer method is simple and has been described in a number of communications;[15,24,162] when nuclei in a position r are acted upon by an additional saturating microwave frequency field, the line intensity corresponding to the nuclear transitions in the position s changes provided that the nuclei are interchanged between these positions. The method is useful in studies of complex chemical exchange, but its application is restricted; the spectral lines corresponding to these positions must be sufficiently remote from one another to avoid the occurrence of beats associated with the two microwave frequencies employed. This difficulty can be readily overcome in ^{13}C NMR spectroscopy (an additional pulse generator is required for this purpose). The method permits the measurement of rate constants smaller by 2–3 orders of magnitude than in ATLS. Questions concerning its use with allowance for the possibilities of modern experimental techniques have been discussed in a number of communications.[163–165]

Kinetic studies employed 2-D spectroscopy, which in many cases constitute an alternative to the saturation transfer method, have been developed in recent years.[166–171] They will probably prove effective in the study of multiparameter exchange but hitherto they have mainly aroused much publicity and have been of a comparative character.

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DNMR, which is at present based on a highly sophisticated experimental technique, is undoubtedly a powerful method for the investigation of stereodynamics, tautomeric transformations, and other chemical exchange processes. In many cases its extensive possibilities make it possible to overcome difficulties in the study of systems with complex exchange. However, this does not resolve the general problem of the uncertainty arising in the use of ATLS and much effort is essential in this field to search for effective methods of analysis of the temperature variations of the NMR spectra.

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Kinetics of the Formation of Adsorption Layers at a Solution–Air Interface

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Studies of the kinetics of the adsorption of surface-active substances (SAS) from solutions have been reviewed. The influence of the chemical structure of the SAS (the length and degree of branching of the hydrocarbon chains and the nature of the polar group) on the mechanism of the adsorption process and the adsorption-kinetic characteristics of the SAS has been analysed. The correlation between the values of the adsorption and desorption rate coefficients and the adsorption equilibrium coefficient has been discussed.
The bibliography contains 119 references.

CONTENTS

I. Introduction 948
II. The theoretical study of the kinetics of adsorption from solutions 948
III. Experimental methods 951
IV. The kinetics of the adsorption of SAS with different structures 952
V. General regular features and correlations 955

I. INTRODUCTION

There has recently been a significant increase in the number of papers dealing with the study of the kinetics of the adsorption of surface-active substances (SAS) at the interfaces between solutions and air or a liquid. The interest in this problem is due to the fact that many processes associated with the adsorption of SAS at these interfaces (the surface separation of substnaces, dispersion, including emulsification, and also foaming, wetting, spreading, etc.) and many surface phenomena in biological systems take place under conditions in which equilibrium between the surface layer and the bulk of the solution is not established. The study of the kinetics of adsorption gives important information on the nature of surface phenomena. It is needed, in particular, for an understanding of the mechanism of the action of SAS in technological processes and the control of their action.

It is known that a considerable time is required to establish the equilibrium surface tension at the freshly formed surface of SAS solutions. Three main mechanisms are considered to be responsible for the delay in establishing equilibrium. Milner[1] suggested that the delay is due to the diffusion of the solute from the volume of the solution to the surface layer (in present-day terms diffusion to the pre-surface layer directly adjoining the surface layer). The concept of a surface barrier decreasing the rate of the transfer of a substance from the pre-surface layer to the surface layer was proposed by Doss.[2] It is considered that another possible factor decreasing the rate of establishment of the equilibrium surface tension is related to processes of reorientation of the adsorbed SAS molecules in the surface layer. Hansen,[3] who first pointed out this possibility on the basis of published data,[4] however concluded that reorientation processes have only a slight influence on the surface tension of solutions of SAS with low molecular weight. A recent review[5] gave bulk diffusion and processes of rearrangement in the surface layer as the main factors determining the rate of decrease of the surface tension.

There are very few monographs or reviews on the kinetics of adsorption at liquid phase interfaces. In addition to the review[5] already mentioned, which deals chiefly with processes of adsorption on a surface undergoing periodic deformation, the only published summaries are in an out-of-date review[6] and a section in a monograph.[7] These reviews make practically no reference to the results of studied published in the Soviet literature.

The aim of the present work is to examine briefly the results of theoretical studies of the kinetics of adsorption from solutions containing one SAS in non-micellar form (mainly at freshly formed non-deformed liquid phase interfaces), to summarise experimental data on the kinetics of the adsorption of SAS at a solution–air interface, and to analyse the principal regular features of this process. Most attention has been paid to the adsorption of SAS of low molecular weight.

II. THE THEORETICAL STUDY OF THE KINETICS OF ADSORPTION FROM SOLUTIONS

A most important stage in the development of the theory of the kinetics of adsorption at liquid phase interfaces was a study[8] which solved in general form the problem of the diffusion of SAS from the bulk of a solution with adsorption at a phase boundary, first formulated in Ref. 9.

The physical picture of the adsorption process can be represented as follows. The initial moment of time corresponds to the formation of a fresh surface (flow of liquid from a nozzle, bubbling, etc.) or the instantaneous removal of SAS from the surface of a solution (for example by means of a moving barrier). At this moment, the concentration of the SAS in the surface layer is equal to its concentration in the bulk. Estimates show[10] that only 10^{-9} s after the moment of formation of the phase boundary, the concentration of SAS in the pre-surface layer decreases practically to zero (with the condition that there is no barrier to adsorption). This produces a concentration gradient, leading to the directed diffusion of the SAS from the bulk to the surface layer. When a surface barrier is present, and also as equilibrium is approached, the difference between the concentrations of the SAS in the pre-surface layer and in the bulk decreases, with a corresponding decrease in the diffusion flux and the rate of adsorption. Thus the kinetics of adsorption at any

moment of time can be determined by solving the diffusion equation if the concentration in the pre-surface layer is known.

For a planer surface, the problem can be written as follows:[8,9,11,12]

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}; \quad x > 0, \; t > 0 \; , \tag{1}$$

$$c = c_0; \quad x > 0, \quad t = 0 \; , \tag{2}$$

$$c = c_0; \quad x \to \infty, \quad t > 0 \; , \tag{3}$$

$$AD\frac{\partial c}{\partial x} = \frac{\mathrm{d}(\Gamma A)}{\mathrm{d}t}; \quad x = 0, \; t > 0 \; . \tag{4}$$

Here, c is the concentration of the SAS; c_0 the concentration of the SAS in the bulk of the solution at the initial moment and under equilibrium conditions; t the time elapsed from the moment of formation of the surface; x the coordinate ($x = 0$ corresponds to the solution–air interface); D the diffusion coefficinet; Γ the dynamic adsorption; and A the area of the surface. Eqn.(4) is the condition for preservation of the quantity of SAS.

A more general formulation of the problem contains instead of Eqn.(1) a convective diffusion equation, and instead of Eqn.(4) equations for the balance of the SAS in the surface layer with allowance for the diffusion and convective fluxes.[11,13]

For a non-deformed surface (A = conts), the boundary condition (4) reduces to the form[8,9]

$$D\frac{\partial c}{\partial x} = \frac{d\Gamma}{\mathrm{d}t}; \quad x = 0, \; t > 0 \tag{5}$$

and for a deformed surface it can be written in the form[11,12]

$$D\frac{\partial c}{\partial x} = \frac{\mathrm{d}\Gamma}{\mathrm{d}t} + \Gamma\nu(t); \; x = 0, \; t > 0 \tag{6}$$

where $\nu(t) = d\ln A/dt$ is the rate of deformation of the surface.

The solution of the problem (1)–(3) and (5) is written in the form[8,14,15]

$$\Gamma = 2c_0\left(\frac{Dt}{\pi}\right)^{1/2} - \left(\frac{D}{\pi}\right)^{1/2}\int_0^t \frac{c(0,\tau)}{(t-\tau)^{1/2}}\,\mathrm{d}\tau \tag{7}$$

where τ is the integration variable.

It can be seen that the most general formulation of the boundary condition for $x = 0$ (Eqns.(4)–(6)) leads to an integral equation relating the values of the adsorption and the concentration of the SAS in the pre-surface layer. The subsequent course of the solution of the problem involves the introduction of additional equations which make it possible to eliminate $c(0, t)$ from Eqn.(7).

Two different approaches have been used. In the first, it is assumed that equilibrium between the pre-surface layer and the surface layer is established very rapidly, and that the rate of the adsorption process is determined exclusively by the rate of diffusion (diffusion mechanism of adsorption). In this case the relationship between the quantities Γ and $c(0, t)$ is given by the adsorption isotherm equation. The second, more general approach takes account of both the rate of diffusion and the rate of establishment of equilibrium between the surface layer and the pre-surface layer (mixed adsorption mechanism). This approach uses adsorption kinetic equations relating Γ and $c(0, t)$ under non-equilibrium conditions. Finally, there is a particular case when the rate of diffusion is high compared with the rate of establishment of equilibrium between the surface layer and the pre-surface layer (kinetic or adsorption mechanism of adsorption). In this case the concentration of the SAS in all parts of the solution (including the pre-surface layer) at any moment of time is equal to c_0. In this case the rate of adsorption is described by adsorption kinetic equations containing c_0 instead of $c(0, t)$.

An expression for the dynamic adsorption Γ for the diffusion mechanism of adsorption can be obtained using, for example, the Frumkin adsorption isotherm[16]

$$bc_0 = \frac{\theta_0}{1-\theta_0}\exp(-2a\theta_0) \tag{8}$$

which effectively describes the equilibrium adsorption of SAS at liquid phase interfaces.[17,18] When it is used for dynamic conditions (that is when $c(0, t)$ and θ are used instead of c_0 and θ_0 respectively), Eqn.(7) gives:[19,20]

$$\theta = \frac{2c_0}{\Gamma_\infty}\left(\frac{Dt}{\pi}\right)^{1/2} - \frac{1}{\Gamma_\infty b}\left(\frac{D}{\pi}\right)^{1/2}\int_0^t \frac{\theta\exp(-2a\theta)}{(1-\theta)(t-\tau)^{1/2}}\,\mathrm{d}\tau \; . \tag{9}$$

In Eqns.(8) and (9), b is the adsorption equilibrium constant; a the interaction coefficient of the SAS molecules in the surface layer; $\theta_0 = \Gamma_0/\Gamma_\infty$ the equilibrium degree of covering of the surface layer; Γ_0 the equilibrium value of the adsorption corresponding to the concentration c_0; Γ_∞ the maximum value of the adsorption (saturated monolayer); and $\theta = \Gamma/\Gamma_\infty$ the degree of covering of the surface layer under dynamic conditions.

Eqn.(9) does not have an analytical solution. It has been obtained only for a linear isotherm.[21] Numerical solutions of Eqn.(9) were obtained in Refs. 22–24 for the Langmuir isotherm ($a = 0$), and in Refs. 19 and 20 for the Frumkin isotherm. In these cases, dimensionless parameters are used, decreasing the number of solutions to be calculated. The problem of the kinetics of adsorption at a growing spherical surface was examined in Refs. 12, 13, 22, 23, 25–27.

The process of the exchange of SAS molecules between the pre-surface layer and the surface layer is described by the Langmuir equation,[28] which gives the total flux of SAS to the surface as the difference between the forward (adsorption) and back (desorption) fluxes. The magnitude of the forward flux is assumed to be proportional to the concentration of the SAS in the pre-surface layer and the fraction of unoccupied surface, and the magnitude of the back flux is assumed to be proportional to the adsorption:

$$I = \beta c(0, t)(1-\theta) - \alpha\Gamma \tag{10}$$

where I is the resultant flux, and β and α the rate constants of adsorption and desorption respectively.

Eqn.(10) provides an additional boundary condition to Eqn.(4) in the solution of Eqn.(1). When there is no deformation of the surface, the magnitude of the flux I is obviously equal to the rate of adsorption:

$$\frac{\mathrm{d}\Gamma}{\mathrm{d}t} = \beta c(0, t)(1-\theta) - \alpha\Gamma \; . \tag{11}$$

For a deformed surface, the rate of adsorption is given by the expression:[11]

$$\frac{\mathrm{d}\Gamma}{\mathrm{d}t} = \beta c(0,t)(1-\theta) - \alpha\Gamma - \Gamma\nu(t) \; . \tag{12}$$

The kinetic equation (11) is applicable only for an ideal surface layer, since for $d\Gamma/dt = 0$ it becomes the Langmuir isotherm. The kinetic equation for the surface layer described by the Frumkin isotherm (8) has the form:[29]

$$\frac{\mathrm{d}\Gamma}{\mathrm{d}t} = \beta c(0, t)(1-\theta) - \alpha\Gamma\exp(-2a\theta) \; . \tag{13}$$

A different form of kinetic equation of this type is given in Ref. 30; other versions of the kinetic treatment of Eqn. (8) are also possible.[31] Eqn. (13) with allowance for isotherm (8) can be rewritten as follows:

$$\frac{d\theta}{dt} = \frac{\beta}{\Gamma_\infty}\left[c(0,t)(1-\theta) - \frac{\theta}{b}\exp(-2a\theta)\right] \qquad (14)$$

where $b = \beta/\alpha\Gamma_\infty$.

Substitution of the magnitude of the concentration in the pre-surface layer, obtained from the solution of the diffusion-kinetic problem (1)–(3) and (5) in Eqn. (11) gives the expression:[14,15,32]

$$\frac{d\Gamma}{dt} = \beta\left[c_0 - \frac{1}{(\pi D)^{1/2}}\int_0^t \frac{d\Gamma/d\tau}{(t-\tau)^{1/2}}\,d\tau\right](1-\theta) - \alpha\Gamma \ . \qquad (15)$$

The same problem can be solved by another method, by the simultaneous solution of Eqn. (7) and the corresponding kinetic equation. Use of Eqn. (14) gives[29]

$$\theta = \frac{2c_0}{\Gamma_\infty}\left(\frac{D}{\pi}\right)^{1/2}\left\{t^{1/2} - \frac{1}{2}\int_0^t \left[\frac{d\theta/d\tau}{L(1-\theta)} + \frac{\theta\exp(-2a\theta)}{bc_0(1-\theta)}\right]\frac{d\tau}{(t-\tau)^{1/2}}\right\} \qquad (16)$$

where $L = \beta c_0/\Gamma_\infty$.

Eqns. (15) and (16) give exact solutions of the diffusion-kinetic problem for the mixed adsorption mechanism. Some results of calculations using Eqn. (16) are given in Refs. 29 and 33.

The adsorption and desorption rate constants appearing in Eqns. (10)–(16) can be specified using the molecular-kinetic approach[14,34] or expressed in terms of transition state theory.[35,36] The constants β and α cannot yet be calculated theoretically, so that the expressions given in the works cited are used only to interpret experimental data.

If the surface barrier is sufficiently high, the rate of adsorption will be determined by the rate at which this barrier is overcome, that is by the actual kinetics of adsorption. In this case, instead of Eqn. (14), it is possible to write:

$$\frac{d\theta}{dt} = \frac{\beta c_0}{\Gamma_\infty}\left[(1-\theta) - \frac{\theta}{bc_0}\exp(-2a\theta)\right] . \qquad (17)$$

From Eqn. (17), for $a = 0$, $\beta = \text{const}$, $\alpha = \text{const}$, and $\Gamma|_{t=0} = 0$ it follows that[37,38]

$$\theta = \frac{bc_0}{1+bc_0}\left[1 - \exp(-t/\tau_0)\right] \qquad (18)$$

where $\tau_a = [\alpha + \beta c_0/\Gamma_\infty]^{-1}$ is the purely adsorption relaxation time. The kinetics of adsorption for the kinetic mechanism on a deformed surface were examined in Ref. 11.

The results of studies of the non-equilibrium properties of freshly formed surface layers are most frequently represented in the form of the dependence of the dynamic surface tension of the SAS solutions on the lifetime of the surface layer. In the case of the diffusion mechanism of adsorption, it is fairly simple to go from the dynamic adsorption to the dynamic surface tension. In this case, it is usually assumed that the relationship between the surface tension and the adsorption under dynamic conditions is described by the same expression as under equilibrium conditions.[3,39] For example, for non-ideal surface layers of SAS, described by the Frumkin isotherm (8), the relationship between the equilibrium decrease in the surface tension π_0 and the adsorption is given by the Frumkin equation of state:[16–18]

$$\Pi_0 = -\Gamma_\infty RT\left[\ln(1-\theta_0) + a\theta_0^2\right] . \qquad (19)$$

Similarly, for dynamic conditions, it is possible to write:

$$\Pi = -\Gamma_\infty RT\left[\ln(1-\theta) + a\theta^2\right] . \qquad (20)$$

The applicability of this assumption is based on the observation of the principle of local equilibrium, which is used in the theory of the diffusion-controlled kinetics of adsorption.[40] The simplest equation for Π for the diffusion mechanism of adsorption is obtained for $\theta \ll 1$:

$$\Pi = 2RTc_0\left(\frac{Dt}{\pi}\right)^{1/2} . \qquad (21)$$

For the kinetic mechanism of the adsorption process, the surface tension is usually also assumed to depend only on the magnitude of the adsorption. In contrast to the case of the diffusion mechanism, however, this approach is approximate, since the secondary chemical potentials are not introduced into the calculation.[40] A difference in the relationships between Π and Γ under equilibrium conditions and under dynamic conditions may be due, for example, to processes of orientation and structure formation in the surface layer, where for identical adsorption the non-oriented layer may have higher values of the surface tension. For solutions of SAS with low molecular weights, this difference apparently does not exceed the uncertainty of the measurements. This can be seen not only from the works already cited[3,4] but also from a comparison of the results of studies[41,42] in which the kinetics of adsorption of sodium dodecyl sulphate were measured using radioactive tracers, and studies[43–45] of the same SAS using the methods of Wilhelmy and the maximum pressure in a bubble. As shown in Ref. 46, the values of the adsorption rate constants calculated form the data in Refs. 41–45, in spite of the introduction of Eqn. (20) for the treatment of the results from Refs. 43–45.

Where the kinetics of adsorption are described by Eqn. (18), Eqn. (20) gives:[38]

$$\Pi = \Gamma_\infty RT\ln\frac{1+bc_0}{1+bc_0\exp(-t/\tau_a)} . \qquad (22)$$

The possibility of calculating dynamic adsorption from the known diffusion and adsorption-kinetic characteristics of SAS (Eqns. (15) and (16)) is a significant achievement of the theory of the kinetics of adsorption. The fact that methods for the theoretical calculation of the constants β and α are imperfect, however, restricts the applicability of the theory described, and raises to prominance the problem of the experimental study of the adsorption-kinetic characteristics of SAS and their dependence on the nature of the substance, the composition of the solution and the surface layer, etc. The use of Eqns. (15) and (16) to calculate the values of the constants β and α from experimental data on the dynamic surface tension of solutions encounters difficulties which are practically impossible to overcome, because of the complex dependence of the constant β on θ and t.

The present author proposed and justified[29,33,47] an approximate model of the mixed adsorption process. According to this model, the rate of adsorption for a fixed degree of covering of the surface layer can be represented as the sum:

$$\frac{1}{d\theta/dt} = \frac{1}{(d\theta/dt)_k} + \frac{1}{(d\theta/dt)_d} . \qquad (23)$$

The subscripts "d" and "k" refer to the diffusion and kinetic mechanisms respectively, and $(d\theta/dt)_d$ and $(d\theta/dt)_k$ are determined from Eqns. (9) and (17).

If the values of the back rates of adsorption appearing in Eqn. (23) are interpreted as the corresponding resistances, the complete resistance to the motion of the molecules of the SAS from the bulk of the solution into the surface layer can be represented as the sum of the diffusion and kinetic resistances. The mixed kinetics of a first-order chemical reaction at a phase boundary are treated similarly.[48]

An advantage of Eqn.(23) is that it can be used to calculate the adsorption-kinetic characteristics of SAS. It makes it possible to use the experimental values of $d\theta/dt$ and the values of $(d\theta/dt)_d$ calculated from Eqn.(9) to determine the rate of adsorption for the kinetic mechanism

$$\left(\frac{d\theta}{dt}\right)_k = \frac{(d\theta/dt)\cdot(d\theta/dt)_d}{(d\theta/dt)_d - d\theta/dt} \qquad (24)$$

and hence the constant β (using Eqn.(17)). The experimental values of the constants β and α obtained by this method are discussed below.

In addition to the two-stage model of the adsorption process (diffusion–adsorption) described above, approaches not involving the introduction of a kinetic equation are also being developed: the surface potential method,[41] equalisation of the chemical potential,[31] and a diffusion method similar to that proposed in Ref.31, in which the surface layer is assigned a lower diffusion coefficient (compared with the bulk).[49]

On the other hand, in an approach proposed by Rebinder,[50] diffusion is ignored, and the decrease in the surface tension is described as a first-order reaction. The resulting expression has the form

$$\sigma = \sigma_0 + B_0 \exp(-kt) \qquad (25)$$

where σ_0 and σ represent respectively the equilibrium and dynamic surface tension of the solution, and k the rate constant. Eqn.(25) is widely used for the treatment of experimental results, and, as shown in Ref.51, is a particular case of Eqn.(22), describing purely adsorption kinetics.

The above discussion cannot claim to cover completely all the problems of the theory of the kinetics of adsorption at liquid phase interfaces. Without departing from the main theme of the review, reference can be made to studies of such important problems as the kinetics of adsorption from multicomponent solutions,[52–55] the kinetics of adsorption accompanied by mass transfer through the phase boundary,[56–58] the kinetics of adsorption and the dynamic surface elasticity for a surface undergoing periodic deformation,[5,59–64] and the kinetics of adsorption from micellar solutions with allowance for the breakdown of the micelles.[65–68]

III. EXPERIMENTAL METHODS

The dynamic surface tension of SAS solutions is studied by methods using oscillating and tapering jets, the shape and weight of a drop, the maximum bubble pressure, propagation of a capillary wave, by Wilhelmy's method, etc. The jet method is also used to measure the dynamic surface electric potential. Direct measurements of dynamic adsorption are made using radioactive tracers. The methods most frequently used can be examined briefly from the viewpoint of their correspondence to the theoretical models described in the previous section.

The theory of the oscillations of a liquid jet, developed by Rayleigh and Bohr,[69] formed the basis of one of the most widely encountered methods, namely the oscillating liquid jet method. The theory developed in Ref.69 took no account of the non-uniformity of the initial rate profile along the cross-section of the jet, or the surface elasticity. Approximate account was taken of these factors comparatively recently.[70–72] Direct experimental studies of the surface velocity of jets of water and SAS solutions,[73,74] and other published data,[71,72] indicate that the calculated values of the surface tension and the lifetime of the surface are insufficiently reliable in direct proximity to the nozzle (the first few oscillations). This explains the large discrepancies in the results obtained for the same systems by different authors.

The method based on the surface electric potential of a liquid jet[4,75] is free from a number of disadvantages of the oscillating jet method; in the determination of the lifetime of the surface and its rate of deformation by this method, however, difficulties arise as a result of the uncertainty of the calculation of the velocity of the surface of the jet, and also because of the Marangoni effect.[73,74] One modification of the jet method is the trough method with measurement of either the surface tension of a flowing film of liquid[76] or its surface electric potential.[4]

In the drop volume method, the correct interpretation of the results of the measurements requires allowance on the one hand for the existence of convective currents in the volume of the drop and on the other hand for the deformation (expansion) of the surface of the drop during its growth. The models of radial[12,23,25–27] and circulating[77] flow of liquid in a growing drop give significantly different expressions for the dynamic adsorption. Since the actual picture of the flow of liquid in a drop is fairly complex, the determination of the mechanism of adsorption and the calculation of the kinetic parameters of adsorption from the experimental values of the dynamic surface tension, obtained by the drop volume method, are associated with appreciable uncertainty, particularly for the diffusion mechanism of adsorption or mechanisms close to it.

The maximum bubble pressure method provides unique possibilities with respect to the time range of the measurements—from 1 ms to 1000 ms and more, which is much greater than for all other methods. The determination of the lifetime of the surface in the range of high frequencies of bubble formation and the nned to take account of the deformation of the surface of the bubble during the measurements are the main problems associated with this method; they were successfully resolved in Refs.78–82. For low values of the time, the uncertainty of the determination σ is ~1 mN m^{-1}, and the uncertainty of the determination of the lifetime is 1 ms.[81] With a comparatively simple method for taking account of the deformation of the surface,[83] it is possible to calculate the adsorption-kinetic characteristics of SAS from the results of measurements of the dynamic surface tension of their solutions.

Slow changes in surface tension are studied by Wilhelmy's method. A fresh surface is created by removing the surface layer of the solution by suction.[84]

A method involving the measurement of the surface tension of a surface expanding at a given rate has been proposed.[85]

The capillary wave method[86,87] and the method of small periodic deformations[63,64] raise the question of whether the mechanisms of adsorption are the same and whether the values of the rate constants of adsorption and desorption, calculated from the results of measurements of the dynamic surface tension by the usual methods, are equal to the values obtained from data on the propagation of a capillary wave or with periodic deformations of the surface. The answer apparently is that they are not. Thus the rate constant for the adsorption of a given SAS in the general case (see section IV) depends on different parameters, including the lifetime of the surface layer with a definite degree of covering. The periodic deformations involving elongation and contraction during the passage of capillary waves or the movement of a barrier influence the structure of the surface layer and hence the values of the constants β and α.

The radioactive tracer method[41,42] gives reliable values of the dynamic adsorption if the correction for the radioactivity of the bulk of the solution is small. This condition is

satisfied to the greatest extent by tritium, which has recently been used to study equilibrium adsorption. In Refs. 41, and 42, however, the range of reliable values of Γ was restricted to $t > 100$ s.

IV. THE KINETICS OF THE ADSORPTION OF SAS WITH DIFFERENT STRUCTURES

Experimental studies of the kinetics of the adsorption of SAS are carried out to investigate the mechanism of the process (diffusion, kinetic, or mixed) and the conditions under which a given mechanism is realised, and also to determine the rate constants of adsorption and desorption (for the kinetic or mixed mechanisms) and their dependence on the chemical structure of the SAS, its concentration, the presence of added substances in the solution, the degree of covering of the adsorption layer, and its lifetime.

In Refs. 46, and 47 an attempt was made to analyse some of these relationships on the basis of an approximate theory of the mixed adsorption process using a comparatively small amount of experimental data published by different authors on the dynamic surface tension of SAS solutions. Recent detailed studies of the kinetics of the adsorption of normal alcohols[81] and sodium alkyl sulphates[88] from aqueous solutions at their interface with air, and other recently published data, not only make it possible to analyse in much more detail the problem of the relationship between the properties of an SAS and its adsorption-kinetic characteristics but also to obtain a number of important results not discussed earlier.

To analyse the adsorption-kinetic characteristics of SAS, only those experimental studies which satisfy the following requirements have been selected from the large number studied: careful preparation and purification of the specimens; detailed information on the equilibrium surface tension of the solutions; and the use of reliable methods to study the dynamic surface tension. The preceding section shows that the last requirement is not satisfied, in particular, by the oscillating jet method, and some of the data obtained by this method were used only for qualitative estimates.

The results of studies of the kinetics of adsorption from solutions of non-ionogenic SAS can be examined first. A large number of papers (see Ref. 81) have been devoted to the study of the dynamic surface tension of aqueous solutions of normal alcohols. The results of studies by the present author using the maximum bubble pressure method,[81] covering a wide range of surface lifetimes (from 0.001 s to 100 s) for aqueous solutions of alcohols with different hydrocarbon chain lengths (from propanol to decanol), can be summarised as follows: in the homologous series of alcohols, with increase in the length of the molecule by one methylene group, the adsorption rate constant increases by a factor of 3–3.5†, that is to the same extent as the adsorption equilibrium constant. The increase in the adsorption rate constant (for 6 or 7 carbon atoms in the alcohol molecule) leads to a change in the adsorption mechanism: the low-molecular-weight alcohols are adsorbed by a kinetic mechanism, and the high-molecular-weight alcohols by a diffusion mechanism. These results for high-molecular-weight alcohols (heptanol and above) for the most part agree with the data in Ref. 89, where the surface electric potential of a liquid jet was used.

The authors of Ref. 90 (maximum bubble pressure method) and Ref. 91 (breaking meniscus method) studied comparatively dilute decanol solutions. Under these conditions, a slower (compared with Ref. 81) decrease in the surface tension with time was observed. Analysis of these results indicates that decanol is adsorbed by a diffusion mechanism at $t < 10$ s, and by a mixed mechanism, with approximately equal diffusion and kinetic resistances, for longer times. The values of the constants β for $t > 10$ s, calculated from the data in Refs. 90 and 91, were found to be much lower than those obtained by extrapolating the values of β for low-molecular-weight alcohols into the range of low values of t.[81] The decrease in the constant β with increase in t, previously observed in Refs. 46 and 47, is a common property of most SAS, and indicates appreciable structural changes in the adsorption layer, as a result of which the disordered orientation of the molecules for short lifetimes of the surface layer is gradually replaced by a more organised structure, which exerts appreciable resistance to the movement of the SAS molecules into the surface layer.

Another explanation for the dependence of the constant β on the lifetime of the surface layer is possible. It is known (see section III) that in all the methods used to study the dynamic surface tension of solutions in the range of short times (jet, drop, and bubble methods), the surface of the solution increases during the measurements, the increase being revealed to a greater extent at low values of t and to a smaller extent at large values of t. Thus the dependence of β on t can also be represented as the dependence of β on the rate of deformation of the surface $\nu(t)$. Since it is known from rheology that the structure of an object depends on the rate of its deformation, the decrease in the constant β with increase in t (decrease in $\nu(t)$) can apparently be attributed not only to a delay in the production of the equilibrium structure of the surface layer but also to a difference in the extent of its breakdown with increase in the surface area.

A mixed mechanism was also detected in a study of the kinetics of desorption from decanol monolayers at a constant surface pressure.[92]

The position of the polar group in the alcohol molecule has some influence on the rate of adsorption. Thus the rate of the decrease in the surface tension is slightly lower in s-octyl and t-hexyl alcohol solutions than in solutions of the corresponding normal alcohols.[93–95]

The kinetics of adsorption of normal acids are similar to those of the corresponding alcohols.[90,96] In particular, for decanoic acid (as for decanol), the published data[90,91,97] indicate a diffusion mechanism of adsorption at $t < 10$ s. The kinetics of the adsorption of undecanoic acid, calculated from the data of Ref. 98 (Wilhelmy's method), are close to purely diffusion kinetics throughout the entire range of lifetimes of the surface layer (from 200 s to 3000 s).

The results of measurements of the modulus of the dynamic surface elasticity of solutions of decanoic acid in the range of angular frequencies 10^{-2}–10^{2} s^{-1} also indicate a diffusion mechanism of adsorption.[64]

The maximum bubble pressure method ($t = 1$–100 s) has been used[99] to measure the dynamic surface tension of aqueous solutions of decyldimethylphosphine oxide ($C_{10}H_{21}PO(CH_3)_2$), dodecyldimethylphosphine oxide ($C_{12}H_{25}PO(CH_3)_2$), and dodecyldimethylamine oxide ($C_{12}H_{25}NO(CH_3)_2$). Comparison of the experimental data with the results of calculations using the diffusion equations showed that in the region of the lowest values of t studied (less than 1–2 s), these substances are adsorbed by a diffusion mechanism, but mixed adsorption kinetics are observed at longer times. This agrees with the results of a study[26] in which the initial slope of the curves on coordinates σ–t, given in Ref. 99, were used to determine the diffusion coefficients; the results showed good agreement with the

†For C_3–C_7 alcohols.

actual values. A detailed treatment of the data of Ref. 99 with a determination of the values of the constants β was carried out in Ref. 46. All the SAS indicated show a decrease in the constant β with increase in the degree of covering by the adsorption layer and increase in its lifetime. As in the case of the normal alcohols, the adsorption rate constants for the alkyldimethylphosphine oxides icnrease with increased length of the hydrocarbon chain.

The kinetics of the adsorption of non-ionogenic SAS with polyethylene oxide hydrophilic groups have been studied.[38,99,100–105] The results of measurements of the dynamic surface tension of aqueous solutions of the dodecyl ethers of heptaethylene glycol and nonaethylene glycol, and the hexadecyl ether of decaethylene glycol, by Wilhelmy's method at $t > 50$ s indicate that these SAS are adsorbed by a diffusion mechanism.[103,104] The same adsorption mechanism is observed for the hexadecyl ether of octaethylene glycol (ring separation method, $t > 600$ s).[105]

In Ref. 100, the kinetics of the adsorption of the dodecyl ethers of hexa-, hepta-, and octaethylene glycols in the range of surface lifetimes 0.05–0.9 s were studied using the dynamic surface electric potential at the surface of a flowing film of solution (the trough method). Assuming that the relationship between the surface electric potential of the solution and the magnitude of the adsorption is the same under dynamic and under equilibrium conditions, the authors cited used the results obtained for the dodecyl ether of hexaethylene glycol to calculate the magnitude of the adsorption.[100] The values of θ which they obtained were found to be lower than those calculated using diffusion theory.

The dynamic surface tension of aqueous solutions of the dodecyl ether of hexaethylene glycol was also measured in Ref. 99 (maximum bubble pressure method, $t = 1–100$ s). Treatment of the results[99] showed that the diffusion mechanism of adsorption is observed at low concentrations of the SAS (less than 0.02 mole m^{-3}) throughout the entire range of lifetimes t. With increase in the SAS concentration, the range corresponding to the diffusion mechanism of adsorption decreases to 5–10 s, and at longer times a mixed adsorption mechanism is observed. To reconcile the results of Refs. 100 and 99, it must be assumed that the slow change in the surface electric potential is related not to the kinetics of adsorption but to the slow relaxation of the structure of the surface layer, which does not influence the surface tension. This relaxation process may be determined by the orientation of the polyethylene glycol fragment of the SAS molecule.

Measurements of the modulus of dynamic elasticity of the surface of aqueous solutions of the dodecyl ethers of hexaethylene glycol and triethylene glycol in the range of angular frequencies $10^{-2}–10^{-1}$ s^{-1} also indicate a diffusion mechanism for the adsorption of these SAS, as in the case of the dodecyl ether of pentaethylene glycol at a very low angular frequency ($10^{-3}–10^{-2}$ s^{-1}).[63]

The degree of branching of the hydrocarbon chain of the molecule of a non-ionogenic SAS has a considerable influence on the adsorption mechanism and on the magnitude of the adsorption rate constant. The results of studies of the dynamic surface tension of aqueous solutions of di-isobutylphenoxyheptaethylene glycol ($[(CH_3)_3C]_2C_6H_3O(C_2H_4O)_7H$) by the maximum bubble pressure method ($t = 2–30$ s)[38] and by the drop weight method ($t = 0.05–2$ s)[101] indicate a kinetic adsorption mechanism. Thus molecules with highly branched hydrocarbon chains are adsorbed much more slowly than those with linear chains. Their adsorption rate constants also decrease more rapidly with increase in the degree of covering of the adsorption layer (in addition to the above SAS, this is also observed for alkyldimethylphosphine oxides and dodecyldimethylamine oxide[99]).

Among anionic SAS, the kinetics of adsorption from solutions have been studied in most detail for sodium alkyl sulphate solutions (see Ref. 88). Detailed studies of the dynamic surface tension of aqueous solutions have been carried out for sodium decyl, dodecyl, and tetradecyl sulphates in the range of surface lifetime 0.001–500 s (maximum bubble pressure method).[88] The mechanism of the adsorption of sodium decyl sulphate is kinetic throughout the entire range of values of t studied, that of sodium dodecyl sulphate is kinetic at $t > 0.005$ s, and that of sodium tetradecyl sulphate is diffusion at $t < 0.005$ s and kinetic at $t > 0.02$ s.

The magnitude of the rate constant of the adsorption of sodium alkyl sulphates decreases as equilibrium is approached, but the dependence of b on t for different SAS concentrations and degrees of covering of the surface layer is given by a single curve. For a more detailed study of the nature of the surface barrier to adsorption, the kinetics of the decrease in the surface tension when various electrolytes and non-electrolytes were added to the solution were studied.[88] The addition of inorganic electrolytes generally leads to an increase in the range of surface lifetimes in which the diffusion mechanism of adsorption is observed, and to an increase in the adsorption rate constant β. Exceptions are also observed, however. Thus the addition of multiply-charged counter-ions at low lifetimes (low degrees of covering of the surface layer) decreases the rate of adsorption, probably because of their structure-forming action on the surface layer of water.

The results of measurements of the constant β in aqueous solutions of sodium alkyl sulphates with and without the addition of inorganic electrolytes are summarised in Fig. 1 in the form of the dependence of β on the adsorption equilibrium constant b. This dependence was given for the first time for a comparatively small number of SAS in Refs. 46 and 47. The adsorption rate constant for a given lifetime of the surface layer in the range $b < 10$ m^3 $mole^{-1}$ increases rapidly with increase in the adsorption equilibrium constant. Further increase in the constant b as a result of an increase in the quantity of added inorganic electrolytes does not lead to an increase in β, because of the specific action of these electrolytes on the structure and properties of the surface layer of water.[88]

The relationship between the kinetics of the decrease in the surface tension of SAS solutions and the structure of the surface layer of water was observed particularly clearly in a study of aqueous solutions of sodium alkyl sulphates containing added normal alcohols with different chain lengths.[88] It was established that for approximately equal (low) concentrations of the added alcohols in the surface layer, low-molecular-weight alcohols (methanol, ethanol, and propanol), which apparently stabilise the water structure, decrease the rate of adsorption, whereas high-molecular-weight alcohols (pentanol, hexanol, heptanol, and octanol), which apparently break down the water structure, increase the rate of adsorption of the sodium alkyl sulphates.

Thus the results of Ref. 88 indicate that the surface barrier to the adsorption of the sodium alkyl sulphates at the solution–air interface is due both to electrostatic repulsion between the adsorbed and adsorbing ions (since it is suppressed by the addition of inorganic electrolytes) and by effects which are probably related to the need to break hydrogen bonds between the water molecules in the surface layer (suppressed by the addition of electrolytes and non-electrolytes which break down the water structure).

In Refs. 53 and 76, Wilhelmy's method on a flowing film of solution (the trough method) was used to study the kinetics of the adsorption of sodium decanoate, dodecanoate, the tetradecanoate in the presence of 0.1 M NaOH in the surface lifetime range 0.01–1.0 s. The use of more accurate values of

the diffusion coefficients of these substances (5.0×10^{-10}, 4.7×10^{-10}, and 4.4×10^{-10} $m^2 s^{-1}$ respectively)[106] instead of the value 2.8×10^{-10} $m^2 s^{-1}$ used in Ref. 53 indicates that sodium tetradecanoate is adsorbed by a diffusion mechanism, and sodium dodecanoate by a mixed mechanism. It is impossible to say anything definite about the mechanism of the adsorption of sodium decanoate, since its adsorption is close to equilibrium in the surface lifetime range studied.

The dynamic surface tension of aqueous solutions of sodium hexadecanoate was studied by the maximum bubble pressure method in Ref. 107. The pH of the medium and the addition of an inorganic electrolyte (0.2 M KNO_3) had a significant influence on the rate of decrease in σ. At pH 8.2, at which the rate of the decrease is a maximum, the kinetics of adsorption in the presence of the inorganic electrolyte are purely diffusion. At other pH values, and also in solutions without an added inorganic electrolyte, adsorption takes place by a mixed mechanism.

The kinetics of the adsorption of sodium di-iso-octyl succinate-1-sulphonate ($C_{20}H_{37}O_4SO_3Na$) were studied in Refs. 78 and 108. In Ref. 78, the maximum bubble pressure method was used (t = 0.01–0.2 s). Analysis of the experimental results shows that sodium di-iso-octyl succinate-1-sulphonate is adsorbed from aqueous solutions by a mixed mechanism throughout practically the entire range of surface layer lifetimes studied. The adsorption rate constant decreases with increase in t and increases when small quantities of sodium chloride are added.

The kinetics of the adsorption of cationic SAS were studied in Refs. 86, 87, 109–112. Analysis of the observed dependence of σ on t for dodecyltrimethylammonium chloride (fluctuating jet method, t = 0.005–0.05 s)[109] leads to the following conclusions: for $t < 0.01$ s, the mechanism of the adsorption of this SAS is diffusion, but at $t > 0.01$ s a mixed mechanism is observed, and the adsorption rate constant decreases with increase in t.

The maximum bubble pressure has been used[110] to study the influence of change in pH (from 7 to 12.5) on the dynamic and equilibrium surrace tension of an aqueous solution of dodecylammonium acetate ($C_{12}H_{25}NH_3COOCH_3$) and of dodecylammonium chloride with and without the addition of sodium acetate. The lowest value of the equilibrium surface tension and the highest rate of decrease in σ were observed at pH 9.85, at which dodecylammonium acetate is hydrolysed (to dodecylamine). In this case, a diffusion mechanism of adsorption is observed at t < 2–3 s, and a mixed mechanism with increase in the lifetime (to t = 100–200 s). The constant β decreases with increase in t. As expected, the addition of small quantities of sodium acetate has no influence on the kinetics of the adsorption of dodecylammonium acetate at pH 9.85, since there is no electrostatic surface barrier in this case.

The dynamic surface tension of aqueous solutions of hexadecyltrimethylammonium bromide has been measured (maximum bubble pressure method, t = 200–3000 s) in the range of values of σ close to equilibrium.[111] Treatment of these

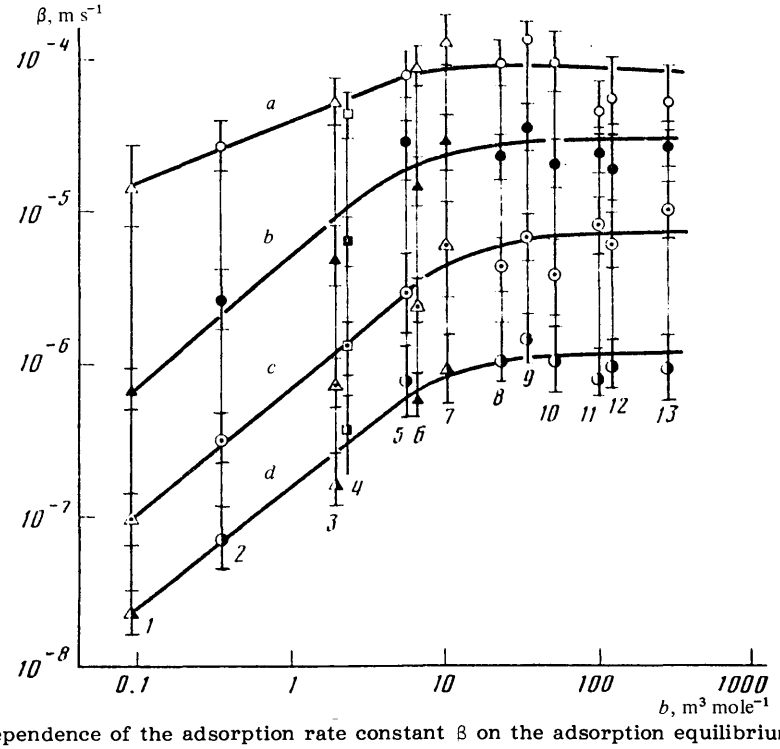

Figure 1. Dependence of the adsorption rate constant β on the adsorption equilibrium constant b for surface lifetimes of 0.01 s (*a*), 0.1 s (*b*), 1 s (*c*), and 10 s (*d*) for sodium alkyl sulphates: *1*) NaDeS in water; *2*) NaDS in water; *3*) NaDeS in 0.1 M NaCl; *4*) NaTS in water; *5*) NaDS in 0.1 M $LiNO_3$; *6*) NaDeS in 0.5 M NaCl; *7*) NaDeS in 0.1 M NaCl; *8*) NaDS in 0.1 M $NaNO_3$; *9*) NaDS in 0.01 M $MgCl_2$; *10*) NaDS in 0.1 M NaCl; *11*) NaDS in 0.3 M NaCl; *12*) NaDS in 0.05 M $MgCl_2$; *13*) NaDS in 0.5 M NaCl; temperature 25°; NaDeS = $C_{10}H_{21}OSO_3Na$, NaDS = $C_{12}H_{25}OSO_3Na$, NaTS = $C_{14}H_{29}OSO_3Na$.[88]

results showed[112] that the mechanism of the adsorption of this SAS is close to kinetic. The adsorption rate constant of hexadecyltrimethylammonium bromide decreases with increase in the lifetime and degree of covering of the surface layer, and is almost independent of the temperature of the solution; this feature, and the decrease in β with increase in temperature for sodium alkyl sulphate solutions,[36,88] indicates that the surface barrier to adsorption has an appreciable entropy component.

The rate constants for the adsorption and desorption of octyl-, decyl-, and dodecylammonium chlorides have also been determined by the capillary wave method.[86,87] The values of β for the cationic SAS, like the value obtained in these studies for the constant β for sodium dodecyl sulphate, are probably too high, because of the destructive action of the capillary waves on the structure of the surface layer, which is thus as it were continuously renewed. The material examined above, however, shows that the values of the constant β are higher for surfaces with a short lifetime than for long-lived surfaces.

Finally, brief mention may be made of the principal results of studies of the kinetics of formation of adsorption layers of polymers. Published data[113–118] indicate that the mechanism of this process is complex and depends on many factors. As a rule, at low concentrations of the polymers in solution at low degrees of covering of the surface layer, the adsorption mechanism is close to diffusion, but with increase in the concentration the role of the surface barrier increases. This last feature is associated with an increasing contribution from electrostatic repulsion forces[113,117] and with structural changes in the surface layer.[116–118] The rate of adsorption of polymers is influenced considerably by the pH of the solution, the presence of inorganic electrolytes, the sign and number of electric charges on the molecule, the hydrophobic character of the SAS, etc. The dependence of the surface tension of polymer solutions on the lifetime of the surface is described satisfactorily by Eqn.(25).

V. GENERAL REGULAR FEATURES AND CORRELATIONS

Comparison of the values of the adsorption rate constants obtained experimentally for different SAS reveals a number of regular features. If the values of β are compared for low or medium degrees of covering of the surface layer and fixed values of t for SAS with alkyl chains R of equal length, it is possible to write the following order of increase in the constant β: $R{-}OSO_3Na < R{-}N(CH_3)_3Cl < R{-}NO(CH_3)_2 < R{-}NH_2 < R{-}COOH < R{-}OH < R{-}PO(CH_3)_2 < R{-}O(C_2H_4O)_6H$.

It should be noted that the surface activity of the substances increases in this order, that is in this case, as in the case of sodium alkyl sulphates (see Fig.1), a correlation is observed between the adsorption rate constant and the adsorption equilibrium constant. It may therefore be expected that the relationship between β and b will not be sensitive to the characteristic features of the chemical structure of the SAS, and for fixed values of θ and t the same relationship will describe all the results obtained. This

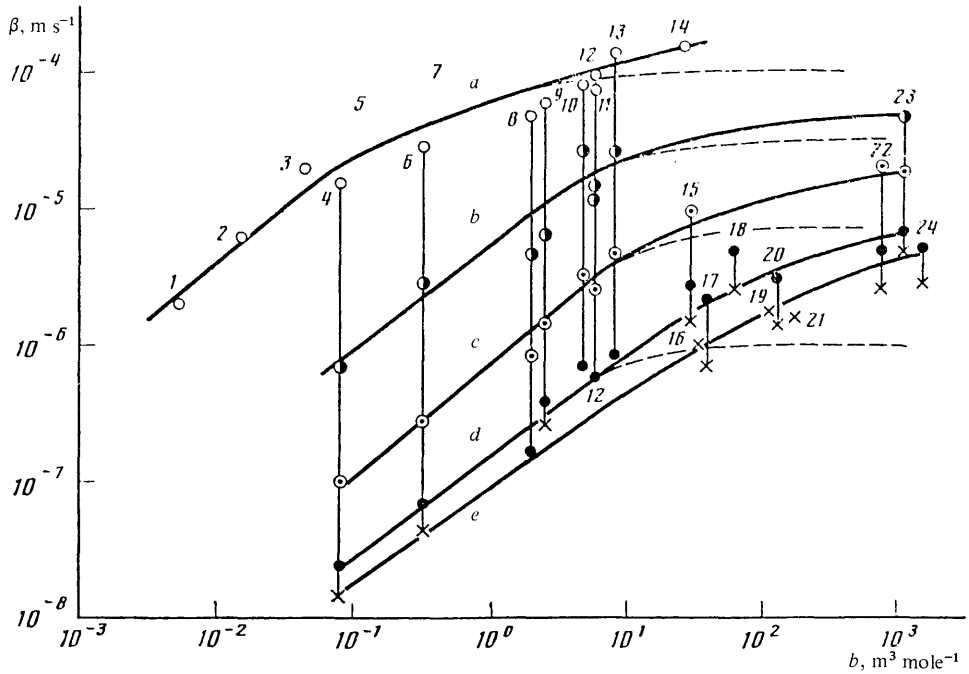

Figure 2. Dependence of the adsorption rate constant β on the adsorption equilibrium constant for surface lifetimes of 0.01 s (*a*), 0.1 s (*b*), 1 s (*c*), 10 s (*d*) and 50 s (*e*) and solution temperatures of 20–25 °C for the following surface-active substances: *1*) C_3H_7OH; *2*) C_4H_9OH; *3*) $C_5H_{11}OH$; *4*) $C_{10}H_{21}OSO_3Na$; *5*) $C_6H_{13}OH$; *6*) $C_{12}H_{25}OSO_3Na$; *7*) $C_7H_{15}OH$; *8*) $C_{10}H_{21}OSO_3Na$ in 0.1 M NaCl; *9*) $C_{14}H_{29}OSO_3Na$; *10*) $C_{12}H_{25}OSO_3Na$ in 0.1 M $LiNO_3$; *11*) $C_{20}H_{37}O_4SO_3Na$; *12*) $C_{10}H_{21}OSO_3Na$ in 0.5 M NaCl; *13*) $C_{10}H_{21}OSO_3Na$ in 1.0 M NaCl; *14*) $C_{12}H_{25}N(CH_3)_3Cl$ in 0.1 M NaCl; *15*) $C_{10}H_{21}PO(CH_3)_2$; *16*) $C_9H_{19}COOH$; *17*) $C_{12}H_{25}NO(CH_3)_2$; *18*) $C_{10}H_{21}OH$; *19*) $C_{10}H_{21}COOH$; *20*) $C_{12}H_{25}NH_2$; *21*) $C_{16}H_{33}OSO_3Na$; *22*) $C_{12}H_{25}PO(CH_3)_2$; *23*) $[(CH_3)_3C]_2C_6H_3O(C_2H_4O)_7H$; *24*) $C_{12}H_{25}O(C_2H_4O)_6H$ (from data in Refs.38, 78, 81, 88, 90, 91, 97–99, 101, 107–110).

relationship for $\beta < 0.5-0.8$ is shown in Fig. 2, which also gives the results obtained for sodium alkyl sulphates with the addition of inorganic electrolytes at $b < 10$ m^3 mole^{-1}; the graphs for $b > 10$ m^3 mole^{-1} in these systems are given by broken lines.

The results given in Fig. 2 show that there is a correlation between the dynamic and equilibrium adsorption characteristics of SAS. For high values of t, the dependence of $\lg\beta$ on $\lg b$ is practically linear throughout the entire range of values of b, whereas for short lifetimes the slope of the curve decreases with increase in b. This is apparently related to the fact that β has a limiting value of $\sim 10^{-2}-10^{-3}$ m s^{-1} (in the complete absence of a surface barrier).[36] In the range in which $\lg\beta$ is linearly dependent on $\lg b$, the following equation is applicable[46,47]

$$\lg\beta = k_1 + k_2 \lg b \qquad (26)$$

where k_1 depends on t, and $k_2 \cong 0.7$.

An interesting feature is that, as noted earlier,[46,47] a similar relationship between the rate constant and the equilibrium constant is observed for a number of chemical reactions, for example reactions involving radicals.[119] There is thus a definite analogy between the kinetics of the adsorption of SAS at a solution–air interface and the kinetics of certain chemical reactions. This analogy provides an additional basis for a chemical approach to the process of adsorption at this boundary, leading, in particular, to the possibility of treating adsorption as an exchange reaction with the formation of an intermediate complex from SAS and water molecules.[81]

It also follows from Fig. 2 that the addition of appreciable quantities of inorganic electrolytes leads to a decrease in the constant β, related to the influence of inorganic electrolytes on the exchange processes in the surface layer.

The results obtained up to the present show that there is a definite relationship between the surface activity of an SAS and the mechanism of its adsorption. Fig. 3 shows the relationship between the adsorption equilibrium constant and the lifetime ranges of the surface layers of different SAS during which these substances are adsorbed by a diffusion mechanism or by a kinetic mechanism. For substances with a low surface activity ($b < 0.1$ m^3 mole^{-1}), the adsorption takes place by a kinetic mechanism throughout the entire range of values of t accessible for measurement. With increase in the surface activity, a certain range of lifetimes appears in which adsorption takes place by a diffusion mechanism, and for substances with a very high surface activity ($b > 1000$ m^3 mole^{-1}), adsorption takes place by a diffusion mechanism throughout the entire range of values of t. For di-isobutylphenoxyheptaethylene glycol (point No. 23 in Fig. 3), the range of the kinetic mechanism of adsorption is anomalously large, and this, as discussed above, is related to the branched nature of its molecule.

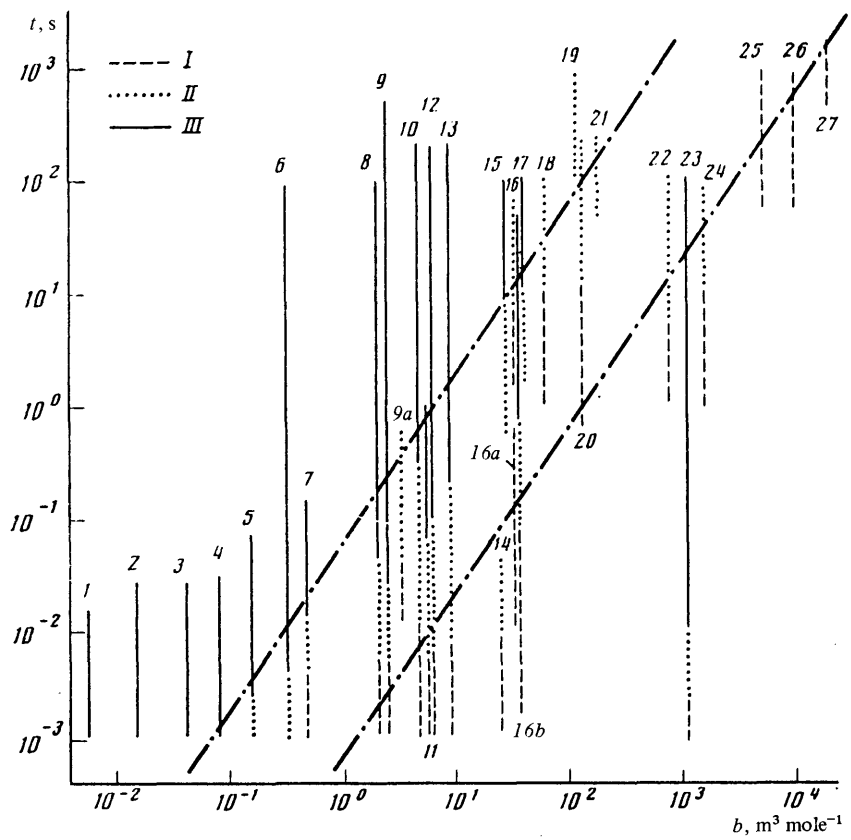

Figure 3. Ranges of different surface-active substance surface layer lifetimes in which diffusion (*I*), mixed (*II*), and kinetic (*III*) adsorption mechanisms are observed. Numbering: *1–24*) same as in Fig. 2; *9a*) $C_{11}H_{23}COONa$ in 0.1 M NaOH; *16a*) $C_{13}H_{25}COONa$ in 0.1 M NaOH; *16b*) $C_{12}H_{25}OSO_3Na$ in 0.01 M $MgCl_2$; *25*) $C_{12}H_{25}O(C_2H_4O)_7H$; *26*) $C_{16}H_{33}O(C_2H_4O)_{10}H$; *27*) $C_{16}H_{33}O(C_2H_4O)_8H$ (from data in Refs. 38, 53, 76, 78, 81, 88, 90, 91, 97–99, 101, 103–105, 107–110).

Fig. 3 contains straight lines which divide the entire field of values of $b-t$ into three regions. To the left of the straight line a the kinetics of adsorption are generally controlled by the surface barrier. The field of values of $b-t$ lying to the right of the straight line b corresponds chiefly to the diffusion mechanism of adsorption, whereas for values of b and t lying between these straight lines, the mixed mechanism predominates. This result is very important, since it makes it possible to predict the mechanism of an adsorption process on the basis of data on the equilibrium adsorption characteristics of SAS.

Since the lifetime of the surface layer determines its degree of covering by SAS molecules, a correlation between the value of the adsorption equilibrium constant and the degree of covering of the surface layer at which a given mechanism of adsorption is realised can be expected. Thus for substances with a low surface activity ($b < 0.1\ m^3\ mole^{-1}$), at least for $\theta > 0.1$, adsorption takes place by a kinetic mechanism, whereas for substances with a high surface activity ($b > 1000\ m^3\ mole^{-1}$), at least for $\theta < 0.9$, adsorption takes place by a diffusion mechanism.

Finally, the correlation between the desorption rate constant α and the adsorption equilibrium constant can be considered. The dependence of α on b can readily be obtained using the data in Fig. 2 and the relationship $b = \beta/\alpha\Gamma_\infty$. The results are given in Fig. 4, and show that the nature of the dependence of α on b is the opposite of the corresponding dependence of β on b. For comparatively weakly surface-active substances ($b < 0.1\ m^3\ mole^{-1}$), the constant α is independent of b. The constant α decreases with increase in b. The decrease in the desorption rate constant is particularly marked for sodium dodecyl sulphate solutions containing large quantities of added inorganic electrolytes (shown by the broken line in Fig. 4), since for these systems, for $b > 10\ m^3\ mole^{-1}$, the constant β does not increase with increase in the surface activity.

The physical significance of the constant α is that it is the probability that the SAS molecule penetrates the surface layer in unit time. Thus the quantity α^{-1} is the time for which the molecule is in the adsorbed state (adsorption time). According to Fig. 4, the adsorption time increases with increase in t, and for a given lifetime and high values of b it increases with increase in the surface activity of the substance.

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To summarise the discussion of studies of the kinetics of the adsorption of SAS at a solution–air interface, it can be concluded that at the present time the main regular features of this process have been outlined, and a number of regular features established, making it possible to advance to reach various conclusions about the characteristic features of the kinetics of the adsorption of a given SAS.

At the same time, a number of problems have not been completely clarified or have not been clarified at all: the influence of the sign and magnitude of the charge and the positions of the polar groups in the SAS molecule on the value of β and on the adsorption mechanism; the relationship between the rate of deformation of the surface and the adsorption-kinetic characteristics of the SAS; the mechanism of processes of structure formation in the surface layer, including processes involving a change in its structure with time; the influence of temperature on the kinetics of the adsorption of different SAS; and the analysis of the energy

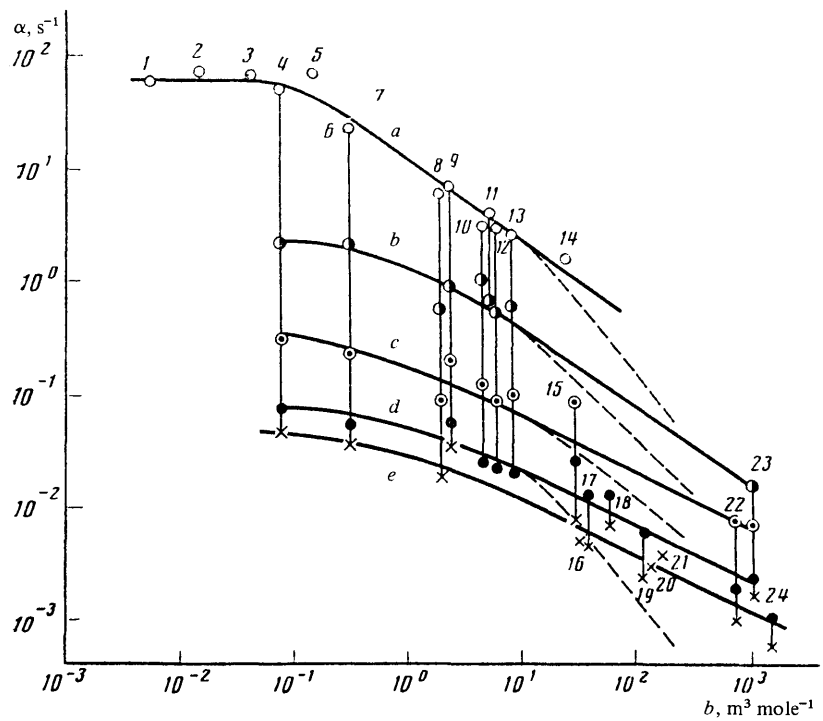

Figure 4. Dependence of the desorption rate constant α on the adsorption equilibrium constant for different surface-active substances. The numbering is the same as in Fig. 2 (from data in Refs. 38, 78, 81, 88, 90, 91, 97–99, 101, 107–110).

characteristics of the transition state. The kinetics of adsorption from multicomponent solutions, and adsorption at a liquid–liquid interface, have been very little studied. The solution of these problems will facilitate the development of the general theory of surface phenomena, will give information on the surface forces, structure, rheology, and intermolecular interactions in adsorption layers, and will provide a basis for the development of new criteria for the synthesis and selection of highly effective SAS and compositions acting under non-equilibrium conditions.

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The Heterogeneous-catalytic Activation of Nitrogen and Oxygen Molecules

G.I.Panov

Data on the activation of molecular nitrogen on metals and metal nitrides have been analysed and compared with the previously observed regular features of the activation of oxygen on oxide catalysts. The similarity in the mechanisms of the isotopic exchange of O_2 and N_2 makes it possible to examine from a single viewpoint questions relating to the prediction of catalytic action in reactions involving these molecules.
The bibliography contains 92 references.

CONTENTS

I. Introduction 960
II. The isotopic exchange of oxygen and reactions involving extensive oxidation 961
III. Nitrides as ammonia synthesis catalysts 962
IV. The kinetics and mechanism of the isotopic exchange of nitrogen 964
V. The molecular form of adsorbed nitrogen 965
VI. The heat of adsorption of nitrogen and the activation energy of the isotopic exchange of N_2 967
VII. The dependence of the catalytic activity in isotopic exchange reactions on the heats of adsorption of nitrogen and oxygen 968
VIII. Estimation of the rate of the synthesis of ammonia from data on the isotopic exchange of N_2 969
IX. The stability of nitrides. Thermodynamic estimations 970
X. Comparison of the experimental and calculated rates of synthesis of ammonia 971

I. INTRODUCTION

A large number of papers have been devoted to the study of the reactivity of oxygen. The results of these studies have been summarised in a number of reviews, including a recently published work[1] dealing with the catalytic activation of oxygen. The activation of nitrogen has been much less extensively studied, although this question is of equal theoretical and practical interest and importance.

In the examination of the problem of the activation of nitrogen, it is necessary first of all to take account of the exceptionally high bond energy in the N_2 molecule, which is greater than the energy of practically all other chemical bonds. This feature creates two difficulties. The first is associated with thermodynamic restrictions, since no other bonds which might be formed by nitrogen are capable of replacing the energy expended in the rupture of the original nitgrogen–nitrogen bond. As a result, the range of thermodynamically "allowed" reactions in which the nitrogen molecule may be involved is very narrow. Apart from metals, hydrogen is practically the only substance with which molecular nitrogen reacts (to give ammonia), although the course of even this reaction is complicated by the equilibrium conditions. The non-existence of a wide range of reactions is the main reason why the chemical properties of the nitrogen molecule have been insufficiently studied.

The second difficulty is kinetic in character, and is related to the need to activate such a strong bond; this can be explained in terms of the concept of energy compensation, formulated in Ref.2. In chemical transformations, bond rupture takes place in the starting materials, making it necessary to overcome a definite energy barrier E, which in the limit may correspond to the sum of the energies of the broken bonds ΣD_i. In fact, however, such high values of E are not observed, since on moving along the reaction path, some of the energy required for the rupture of the old bonds is compensated by the energy liberated in the simultaneous formation of new bonds. The extent of the compensation is the decisive factor determining the rate of a chemical reaction.

It is this phenomenon that reveals the essential feature of catalytic action. The catalyst, forming part of the activated complexes of the principal stages, increases the degree of compensation η

$$\eta = \frac{\sum D_i - E}{\sum D_i}$$

and thus lowers the activation energy of the reaction.[2] It is clear that the higher the energies of the bonds involved in the reaction, the more efficient the catalyst must be from the viewpoint of energy compensation in order to ensure a given reaction rate. Thus for example in the dissociative adsorption of a molecule A_2, the activation energy of adsorption will represent the non-compensated part of the dissociation energy $D(A_2)$:

$$E = (1 - \eta) D(A_2) ,$$

Thus for equal values of η, the activation energy of the adsorption of nitrogen will be almost twice that of oxygen, in view of the corresponding difference in the values of $D(N_2)$ and $D(O_2)$ (Table 1). This probably also explains the fact that there are only a few catalysts capable of activating nitrogen, whereas catalytic properties in reactions involving molecular oxygen are shown by a wide range of different chemical substances.[3]

The activation of molecules in a reaction is usually due to a weakening of a bond as a result of electron transfer in a particular direction. From this viewpoint, however, the positions of the orbitals in the nitrogen molecule are extremely unfavourable. The energy of the highest occupied orbital is −15.3 eV, which corresponds to the exceptionally high ionisation potential of the nitrogen molecule (1500 kJ mole^{-1}). On the other hand, the nitrogen molecule has a high first

unoccupied orbital, and electron transfer to this orbital is also energetically unfavourable, since it requires the expenditure of 352 kJ mole^{-1}.[4] It is thus difficult to bring N_2 into a reactive state either by transferring electrons to the molecule or by withdrawing electrons from it.

The values of the dissociation energies (D), ionisation potentials (I), and electron affinities (A) for the N_2 and O_2 molecules[5] are compared in Table 1.

Table 1. Characteristics of the nitrogen and oxygen molecules.

Molecule	D, kJ mole^{-1}	I, kJ mole^{-1}	A, kJ mole^{-1}
N_2	942	1500	−352
O_2	494	1163	42

The activation of nitrogen is particularly important in the synthesis of ammonia. Because of its great practical interest, the synthesis of ammonia is one of the few reactions which has attracted the close attention of scientists over a long period of time. There is hardly another reaction for which such a large number of varied catalysts has been tested.

If reference is made strictly to the activation of nitrogen, however, the synthesis of ammonia can hardly be regarded as a comprehensive test reaction. In the first place, in this case it is necessary to activate not only nitrogen but also hydrogen. In the second place, as shown below, some catalysts which are able to convert the nitrogen molecule into a reactive state are unstable in the presence of H_2, although their study is extremely important for an understanding of the general features of the activation of nitrogen.

From this viewpoint, a unique position is occupied by the method of isotopic exchange, which makes it possible to study the activation of molecules of a given kind in "pure" form, without the introduction of any additional components into the system. When applied to a diatomic gas, this method requires the study of two independent reactions taking place under conditions of adsorption equilibrium or hetero-exchange, that is the redistribution of the isotopes between the surface (s) and the gas phase:

$$^{15}N^{15}N+{}^{14}N_s\rightarrow{}^{14}N^{15}N+{}^{15}N_s$$

and homomolecular exchange, that is the redistribution of the isotopes between molecules of the gas phase:

$$^{14}N^{14}N+{}^{15}N^{15}N\rightarrow 2{}^{14}N^{15}N\ .$$

This raises the important question of whether the activation of nitrogen with respect to these simplest reactions is typical of its activation with respect to other reactions, in particular the synthesis of ammonia. The very first study by Taylor[6] in 1939 detected a qualitative relationship; it was found that the isotopic exchange and the synthesis of ammonia take palce in the same temperature range. Subsequent studies confirmed repeatedly that catalytic activities in the reactions of isotopic exchange and the synthesis of ammonia always change in the same sense.[7,8] Isotopic exchange has been little used to study the activation of nitrogen, and has been used chiefly to investigate the mechanism of the synthesis of ammonia. Thus most published studies have been carried out using iron or promoted iron catalysts, which are the most active and whose practical value far exceeds that of all other catalysts.

The fact that there have been insufficient systematic studies probably explains the absence of reviews of the isotopic exchange of nitrogen, apart from the brief summaries in Refs.8 and 9. This is probably also related to a large extent to the low reliability of the results, particularly those obtained in the study of metals. This last feature is due primarily to the fact that metallic catalysts, both in the synthesis of ammonia and more particularly in isotopic exchange, are very sensitive to the degree of preliminary reduction and to the presence of oxygen-containing poisons.[10-12]

The catalytic properties in the isotopic exchange of N_2 have been studied not only for Fe but also for the following metals: Cr, Co, Ni, Cu,[7] Mo,[13-15] Ru,[16,17] Ta,[18] W,[6,14,19] Re,[14,20] and Os.[21] Many of the studies are qualitative in character, and give information only on the temperature range in which exchange was observed. Reliable data which might be reduced to comparable conditions have apparently been obtained only in a few comparatively recent studies and are restricted to two metals, Fe[10,17,22] and Ru.[17]

More reliable data on the isotopic exchange of N_2 have been obtained on metal nitrides. In addition to Mo_2N, studied earlier,[22] a fairly wide range of nitrides, including those of Li, Cu, the alkaline earth metals, the lanthanides, and uranium have now been studied in this reaction. Compared with metals, it is easier to obtain reliable results using nitrides, since these catalysts are not highly sensitive to the presence of oxygen-containing poisons.[23-25]

Thus a fairly large amount of experimental material has now been published, and in subsequent sections an attempt will be made to analyse this material and to compare it with the regular features previously established for the activation of O_2 on oxides.

II. THE ISOTOPIC EXCHANGE OF OXYGEN AND REACTIONS INVOLVING EXTENSIVE OXIDATION

Extensive isotopic-exchange studies of the activation of molecular oxygen on metal oxides have been carried out.[1,26-30] These studies have played a decisive role in establishing the regular features of extensive oxidation reactions. Rigorous kinetic equations have been derived for the redistribution of the isotopes in simultaneous hetero-exchange and homo-exchange,[31-33] and these have stimulated considerably the subsequent development of the method.

Depending on the number of surface oxygen atoms taking part in the exchange act, three types of exchange are possible in an M–O_2 system: 1) without the participation of surface oxygen, 2) with the participation of one surface oxygen atom, and 3) with the participation of two surface oxygen atoms. Analysis of the kinetic relationships makes it possible to calculate the rates for these types of exchange (w_1, w_2, w_3), which are related to the observed rates of hetero-exchange, w_r, and homo-exchange, w_k, as follows:[31-33]

$$w_r=w_2/2+w_3 \qquad (1)$$

$$w_k=w_1+w_2+w_3\ . \qquad (2)$$

All three types of exchange are observed on oxides under different conditions, but the case of greatest interest for catalysis corresponds to the mechanism of exchange of the third type, which is the predominant type (and often the only type) at high temperatures, that is the range in which

oxidative reactions take place. This exchange is limited by the equilibrium dissociative adsorption and desorption of oxygen, and it can be regarded as resulting from the reversible dissociation of a surface layer of the oxide. From Eqns.(1) and (2), for the third typd of exchange, $w_r = w_k$.

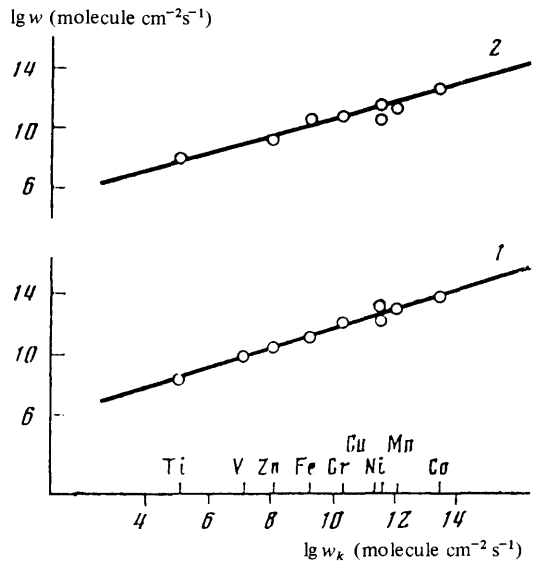

Figure 1. Comparison of the rates of the oxidation of hydrogen (*1*) and methane (*2*) with the rate of the isotopic exdhange of oxygen w_k on oxides.[34]

Comparison of the catalytic properties of a wide range of oxides in the isotopic exchange of O_2 and in extensive oxidation reactions showed changes in the same sense, illustrated in Fig.1. This is a general relationship, and is observed for the oxidation of not only hydrogen and methane, but also CO, NH_3, acetylene, benzene, and other substances.[34] Subsequent studies established the essential features of this relationship. Thus the nature of the limiting stage is the same in all cases, and, as in isotopic exchange, is related to the removal of oxygen from the catalyst surface.[35] Although the rates of the oxidation of different substances may differ considerably, the same regular feature is always observed: the activation energy of the reaction is lower, and its rate higher, the smaller the heat of adsorption of oxygen $q(O_2)$ on the catalyst surface:

$$E = E_0 + \alpha q(O_2) \,. \qquad (3)$$

Eqn.(3) shows that a certain fraction α of the heat of adsorption appears in the activation energy of extensive oxidation E. This regular behaviour is also seen in oxidative reactions on catalysts of other types, in particular metal carbides.[36]

The strength of the bond formed by oxygen with the catalyst surface also plays an important role in reactions of partial oxidation.[3,37]

The dependence of the activation energy of isotopic exchange $E(O_2)$ on $q(O_2)$ is even more direct than in the case of oxidative reactions. It can be seen from Fig.2 that for oxides characterised by the third type of exchange, the equality $E(O_2) = q(O_2)$ is observed, and this makes the isotopic-exchange method particularly effective for the study of the reactivity of surface oxygen, since it makes it possible to characterise quantitatively the heat of adsorption of O_2.

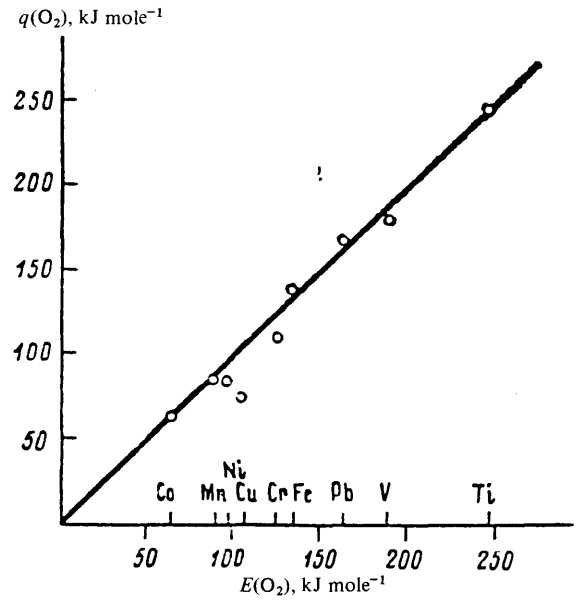

Figure 2. Relationship between the activation energy of isotopic exchange and the heat of adsorption of oxygen on metal oxides.[28]

The dependence of the rate and the pre-exponential factor for isotopic exchange on the heat of adsorption of oxygen is shown in Fig.3 (from the data in Refs.38 and 39).

The regular features observed make it possible to use data on the isotopic exchange of oxygen to predict the catalytic properties of oxides in extensive oxidation reactions and make it of considerable interest to attempt to establish a corresponding relationship between the isotopic exchange of nitrogen and the synthesis of ammonia.

III. NITRIDES AS AMMONIA SYNTHESIS CATALYSTS

Attempts to use metal nitrides as catalysts for the synthesis of ammonia were made as early as the end of the last century.[40] In the early studies, insufficient attention was paid to the phase and chemical composition of the specimens after the experiments, and the catalytic activity was usually attributed to the metal.[41] Subsequent studies showed that under the conditions of the synthesis of ammonia, some metals are converted into their nitrides, among which uranium nitride was found to be a highly active catalyst.[42] It was on uranium nitride, and also on metallic osmium, that Haber was first able to obtain high yields of ammonia which left no doubt about the promising possibilities provided by the catalytic method for the synthesis of NH_3.

Since the nineteen-sixties, there has been an increase in interest in nitrides as ammonia synthesis catalysts. This has also been related to the problem of the applicability of ideas about the mechanism of the synthesis, developed mainly in the study of iron catalysts, to catalysts of other classes. The

basic information on the catalytic properties of nitrides in the synthesis of NH_3, obtained since 1960, is given in Table 2. The data for a doubly promoted iron catalyst are also given for comparison. It can be seen that most of the nitrides studied are transition metal nitrides. The interest in nitrides of this class is related to the fact that transition metals and their compounds usually show an increased catalytic activity in redox reactions.[49,50]

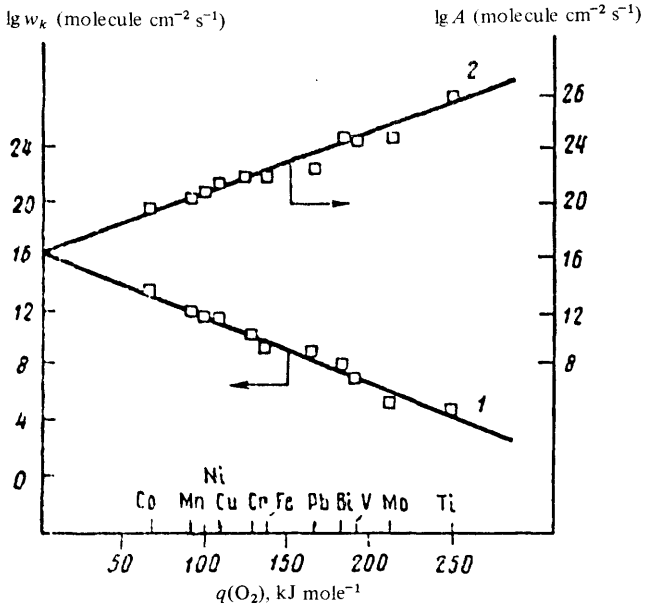

Figure 3. Dependence of the rate (*1*) and the pre-exponential factor (*2*) for the isotopic exchange of O_2 on oxides at 573 K and a pressure of 1.33 kPa on the heat of adsorption of oxygen.

The reaction of ammonia synthesis is reversible, and its rate is considerably reduced by ammonia. This makes it difficult to compare the activities of different catalysts. For a quantitative comparison it is often necessary to have data on the values of the rates at the same temperature, pressure, and NH_3 concentration at the outlet from the reaction vessel.[51] For the nitrides studied, this comparison in many cases is impossible, because of the large differences in the NH_3 concentration. Nevertheless, it is qualitatively clear that all the nitrides given in Table 2, including transition metal nitrides, with the exception of UN_x, have a low catalytic activity. The most active of them, Mo_2N, to which the largest number of studies has been devoted (including Ref. 52, where it was observed for the first time that the ammonia synthesis mechanisms on Mo_2N and on an iron catalyst are the same), is much less active than promoted iron.

A noteworthy feature is the large difference in the rates of ammonia synthesis on uranium nitride. The α-U_2N_3 specimen studied in Ref. 47 was found to be less active by several powers of ten than the UN_x specimen studied by Haber.[42] Similar differences were observed in the study of the isotopic exchange of N_2.[53] An α-U_2N_3 specimen prepared by the direct reaction of the metal with nitrogen at 972 K was also found to be 10^4–10^5 times less active than a specimen with the composition $UN_{1.70}$, prepared under milder conditions by nitriding the hydride, previously obtained from the metal. The values of the heat of adsorption of nitrogen on these specimens differ by 120 kJ mole^{-1}. This marked dependence of the adsorption and catalytic properties of uranium nitride on the chemical composition for similar crystal structures is extremely unusual, and its explanation requires further studies.

Table 2. The synthesis of ammonia on metal nitrides at 673 K.

Catalyst	s, m^2 g^{-1}	p, kPa	[NH_3], vol.%	$10^{-10}\,w$, molecule cm^{-2} s^{-1}	Refs.
BN *	—	98	—	—	[43]
Ti_2N	0.21	98	$6.6\cdot10^{-4}$	6.2	[43]
TiN	0.44	98	$2.0\cdot10^{-4}$	0.9	[43]
VN	0.32	2250	$1\cdot10^{-3}$	0.3	[44]
Cr_2N	0.1	98	$2.8\cdot10^{-3}$	5.5	[43]
CrN	0.06	98	$5.4\cdot10^{-5}$	0.2	[43]
FeN **	—	98	—	—	[45]
Ge_3N_4 **	—	98	—	—	[43]
ZrN	0.08	98	$5.3\cdot10^{-4}$	13	[43]
NbN	0.06	98	$2.0\cdot10^{-4}$	0.9	[43]
Mo_2N	13.5	20	—	0.8	[46]
Mo_2N	2.7	98	$1.2\cdot10^{-2}$	8.9	[43]
Mo_2N ***	5.0	98	$5.4\cdot10^{-2}$	150	[22]
HfN	0.06	98	$2.0\cdot10^{-4}$	8.9	[43]
UN_x	—	9600	2,5	920****	[42]
α-U_2N_3	4.1	2940	$2.5\cdot10^{-2}$	4.9	[47]
Fe *****	10.5	98	$1.85\cdot10^{-1}$	67	[48]

Symbols: s is the specific surface, p the pressure of the stoichiometric mixture, [NH_3] the ammonia concentration, and w the rate of the synthesis of ammonia.
*Inactive.
**Decomposes.
***At 748 K.
****Approximate estimate.
*****Doubly promoted iron catalyst.

The attention of research workers has recently been drawn to the so-called ionic nitrides, formed by the electropositive elements of groups I, II, and III of the periodic system.[54] These elements have an increased reactivity with respect to nitrogen. Of particular interest is lithium, which is the only element that reacts vigorously with N_2 even at room temperature to give the phase Li_3N.

Various alkaline earth metals (Ca, Sr, Ba) react with nitrogen to give not only the nitrides M_3N_2 but also other stable compounds, namely the subnitrides (M_2N) and pernitrides (M_3N_4, MN_2), which show a number of interesting properties. In the subnitrides, the bonds between the metal atoms are partly preserved, as indicated by the metallic character of their electrical conductivity,[55,56] so that these compounds are similar to the metal-like nitrides of the *d* elements. The pernitrides, on the other hand, contain an N–N bond, so that the hydrolysis of these compounds leads to the partial liberation of hydrazine instead of NH_3. The possibility of obtaining hydrazine by this method probably stimulated a number of studies of the physicochemical properties of nitrogen-containing compounds of the alkaline earth elements.[57–59]

The possible formation of various chemical compounds with nitrogen suggests that the nitrides of this class may be interesting materials from the viewpoint of the activation of molecular nitrogen. Their study has followed two directions: 1) the study of the activation of molecular

nitrogen and its state on a surface by isotopic exchange;[24,25,60-63] 2) the study of the synthesis of ammonia as a reaction for which the activation of nitrogen is the limiting stage.[25,53,61]

These studies open up the possibility of determining how general are the regular features established for oxides, molecular oxygen, and oxidative reactions, and whether they are applicable to other reactions and systems.

The subsequent analysis, in addition to ionic nitrides, will also consider catalysts based on Fe,[22] Ru,[17] and Mo_2N,[22] for which sufficiently reliable data on the isotopic exchange of N_2 and the synthesis of NH_3 are available. Among the catalysts based on Fe and Ru, the examination will be restricted to the simplest systems consisting of metallic iron and ruthenium without promoting additives.

IV. THE KINETICS AND MECHANISM OF THE ISOTOPIC EXCHANGE OF NITROGEN

The nitrides of the metals of groups I, II, and III of the periodic system are most frequently understood to be the stoichiometric compounds with the compositions M_3N, M_3N_2, and MN respectively.[54,64] Detailed studies have shown, however, that in a number of cases these compounds cannot be obtained at all.[65] Table 3 shows that the stoichiometry of the nitrides in fact does not always correspond to the composition expected on the basis of classical ideas. Moreover, some of these nitrides (strontium and barium nitrides and uranium nitride with the approximate composition $UN_{1.70}$) in general have a variable chemical composition, which changes considerably with change in the conditions.[53,60]

Table 3. Kinetic characteristics of the isotopic exchange of nitrogen (573 K, 52 Pa).

Catalyst	Crystal structure		x_v	x_{exch}	n	$E(N_2)$, kJ mole^{-1}	lg w (molecule cm^{-2} s^{-1})	lg A	Refs.
	type of lattice	a, Å							
Li_3N	cubic	5.50	1.0	x_v	0.4	175	6.9	23.0	[66]
Cu_3N *	cubic	3.815	—	—	—	—	—	—	[66]
$MgN_{0.6}$**	FCO	9.9525	—	—	—	—	—	—	[25]
$CaN_{0.5}$	anti-Mn_2O_3	11.463	0.6	0.7	0.7	130	8.0	20.0	[25]
$SrN_{0.5}$	—	—	0.8	60	0.8	55	11.4	16.3	[66]
$BaN_{0.6}$	—	—	0.7	50	0.7	50	11.3	15.9	[60, 62]
LaN	NaCl	5.288	~0.1	0.5	—	—	—	—	[25]
CeN	NaCl	5.021	1.0	3.0	0.5	130	8.0	19.8	[24]
PrN	NaCl	5.151	~0.1	0.5	—	—	—	—	[61]
ErN	NaCl	4.84	~0.1	0.3	—	—	—	—	[61]
α-U_2N_3	Mn_2O_3	10.644	1.0	x_v	0.5	225	4.4	24.9	[63]
$UN_{1.70}$	CaF_2	5.30	0.9	x_v	0.5	105	10.0	19.9	[53]
Mo_2N	—	—	1.0	x_v	0.5	155	6.3	20.8	[22]
Fe	—	—	1.0	—	0.5	130	9.4	21.2	[22]
Ru	—	—	—	—	0.7	125	7.6	19.0	[17]

Symbols: x_v is the quantity of nitrogen in the catalyst specimen, A is the pre-exponential factor.
*Decomposes.
**Inactive up to 973 K.

The principal results of studies of the kinetics and mechanism of the isotopic exchange of nitrogen can be summarised (Table 3). In general, all three possible types of exchange are observed on nitrides. As in the case of oxides, however, the change by the third type of mechanism most frequently predominates (its proportion $\kappa = w_3/w_k$ is equal or close to 1). Thus exchange takes place chiefly as a result of the reversible dissociation of the surface layer of the nitride. Exceptions are the nitrides of lanthanum, praseodymium, and erbium, which have a very low catalytic activity and have not been studied in detail.

The same regular feature is also observed for metallic catalysts. The isotopic exchange on Fe takes place only by the third type of mechanism.[22] A detailed analysis of the kinetics of exchange on Ru has not been carried out, but the similarity in the rates of hetero-exchange and homo-exchange indicates that the third type of exchange also predominates in this case.[17]

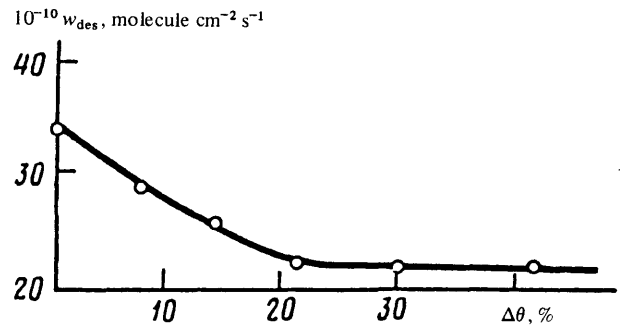

Figure 4. Dependence of the rate of desorption of nitrogen at 593 K on the quantity of nitrogen removed from the surface of $BaN_{0.62}$ (% of a monolayer).

Many nitrides, particularly those with variable chemical composition, show a high mobility of the nitrogen atoms in the crystal lattice. Thus for Sr and Ba nitrides,[60] the quantity of nitrogen taking part in exchange, x_{exch}, amounts to 50–60 surface monolayers at 550 K. This means that the "movement" of nitrogen to a depth of several tens of monolayers takes place more rapidly than exchange between the surface and the gas phase. In the case of the nitride $UN_{1.70}$[53] at this temperature, the exchange involves all the nitrogen of the solid phase ($x_{exch} = x_v$). The high rate of self-diffusion of nitrogen makes it impossible to determine whether the surface is uniform or non-uniform, since in either case the rapid movement means that the nitrogen on all parts of the surface acquires an equal probability of exchanging with the gas phase. The very fact that rapid movement takes place, however, indicates that if there is any non-uniformity, it can hardly be clearly defined. This is confirmed by experiments on the desorption of nitrogen from a barium nitride surface, the results of which are given in Fig. 4.[62] The rate of desorption shows an extremely weak dependence on the quantity of nitrogen removed, and after 20% of the nitrogen of the surface monolayer has been removed, its subsequent removal does not lead to any decrease in the rate of desorption. This is related to the fact that, as a result of the high rate of diffusion, a change in the degree of surface covering is compensated by the migration of nitrogen from the bulk of the $BaN_{0.62}$.

According to Ref. 67, self-diffusion also takes place at a high rate in the adsorbed layer of nitrogen on the surface of a promoted iron catalyst. For oxides, the mobility of oxygen is less characteristic. Among oxides, however, there are

also catalysts (MoO_3, V_2O_5) in which movement takes place throughout the entire volume, although this occurs at much higher temperatures.[28]

The kinetic order n of the exchange of nitrogen can be considered. For oxygen on oxides characterised by the third type of exchange, the order of the reaction is generally close to 0.5.[68] Table 3 shows that this regular feature is also observed for nitrogen. This pressure dependence was explained[68] by assuming that the limiting stage of the third type of exchange is the reversible dissociative adsorption of nitrogen

$$N_2+[\ ]+(\ )\rightleftarrows[N]+(N) \qquad (4)$$

to give firmly bound [N] and weakly bound (N) surface forms. These forms are present in equilibrium, as a result of rapid transformation:

$$[N]+(\ )\rightleftarrows[\ ]+(N)\,.$$

Since isotopic exchange takes place under conditions of adsorption equilibrium, the rate of exchange w_3 can be expressed as the rate of adsorption or desorption, and, in accordance with Eqn.(4), is described by the expression

$$w_3=k_a p(1-\theta_1)(1-\theta_2)=k_d\theta_1\theta_2 \qquad (5)$$

where p is the nitrogen pressure, and k_a and k_d the rate constants of adsorption and desorption respectively.

Assuming Langmuir adsorption at a high degree of covering of the surface by the firmly bound form ($\theta_1 \cong 1$) and a low degree of covering by the weakly bound form ($\theta_2 \ll 1$), it follows from Eqn.(5) that

$$w_3=\frac{k_a}{b_1^{0.5}}p^{0.5}$$

where b_1 is the adsorption coefficient for the firmly bound form. This dependence of the reaction rate on the nitrogen pressure corresponds to the experimentally observed order of the exchange reaction by the third type of mechanism.

A detailed explanation was also given in Ref.69, where it was assumed that the exchange takes place via the following stages:

$$N_2+[\ ]\rightleftarrows[N_2] \qquad (6)$$

$$[N_2]+[\ ]\rightleftarrows 2[N]\,. \qquad (7)$$

If stage (6) is slow, this also leads to a reaction of order 0.5 with the condition that $\theta[N_2] \ll 1$ and $\theta[N] \cong 1$. The assumption that molecular adsorption is the rate limiting stage can hardly be correct, however.

The higher orders observed on various nitrides, and also on metallic ruthenium, can probably be attributed to additional contributions from the mechanisms of the first and second types.

Thus there is an extensive analogy between the mechanism of the exchange of N_2 and O_2. The specific features of N_2, however, are superimposed on its exchange and a number of characteristics, revealed chiefly at low temperatures. An example is provided, in particular, by the so-called low-temperature exchange.

Most oxides, previously subjected to vacuum treatment at 673–873 K, after cooling are capable of bringing about homomolecular exchange by the first type of mechanism at a high rate. This exchange, which takes place with a very low activation energy, is due to the existence of anion vacancies on the surface and is observed at reduced temperatures down to liquid-nitrogen temperature. The mechanism of the low-temperature exchange probably involves a redistribution of the bonds in a four-atom complex consisting of two adsorbed diatomic molecules.[1] There is only a very small quantity of oxygen in the molecular form on the oxide surface, and it generally cannot be detected experimentally.

In the case of nitrides, the formation of anion vacancies as a result of the removal of nitrogen on high-temperature vacuum treatment does not lead to low-temperature exchange. It cannot be observed on metallic catalysts either.[70] This is apparently due to the much greater stability of the N_2 molecule, compared with O_2, which makes a redistribution of the bonds between nitrogen atoms in the low-temperature range impossible.

This is also probably responsible for another characteristic feature of nitrides. Some of them, namely Sr_2N and $BaN_{0.62}$, at low temperature are capable of binding a considerable quantity of nitrogen in the molecular form,[62] and the state of this nitrogen will be examined in the next section.

V. THE MOLECULAR FORM OF ADSORBED NITROGEN

Comparison of the rates of the separate stages with the rate of the catalytic process as a whole provides an effective method for studying the mechanism of reactions, and is particularly widely used in the study of oxidative processes.[71] The homomolecular exchange of nitrogen involves the following stages: adsorption; surface processes leading to a redistribution of the isotopes: and desorption.

Isotopic exchange is studied under conditions of adsorption equilibrium, when the rates of the adsorption and desorption stages are equal. The ratio between the rate of the reversible adsorption (desorption) and the rate of the surface processes is one of the factors determining the reaction mechanism. It was the comparison of the rate of desorption with the rate of isotopic exchange that made it possible to establish an interesting characteristic feature of Sr and Ba nitrides with respect to molecular nitrogen.[62]

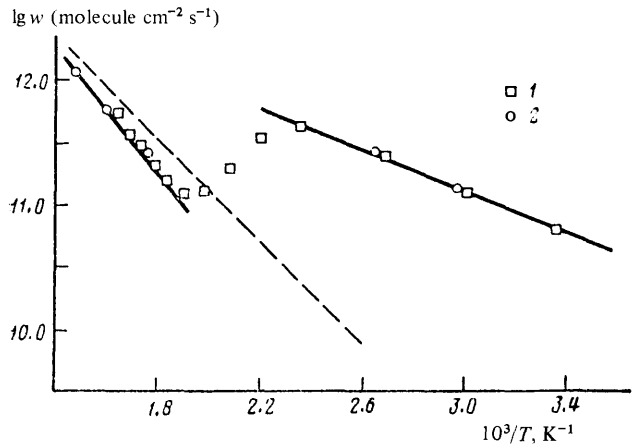

Figure 5. Temperature dependence of the rates of the desorption (*1*), hetero-exchange (*2*), and homo-exchange (broken straight line) of nitrogen on barium nitride.[62]

Fig.5 gives the temperature dependence of the rate of the desorption of nitrogen from the surface of $BaN_{0.62}$. The rate of desorption corresponds to the equilibrium degree of covering of the surface at the temperature of the experiment and a

nitrogen pressure of 52 Pa, that is it was measured for the same state of the surface as the rate of exchange. It is possible to distinguish three ranges in which this dependence has different forms: the high-temperature range (525–608 K), where the rate of desorption coincides with the rate of hetero-exchange; the low-temperature range (300–425 K), where the rate of desorption is 10–100 times the rate of homo-exchange; and the intermediate range, in which the rate increases with decrease in temperature. The explanation for this form of the dependence is that in addition to the atomic form of nitrogen, which is involved in the exchange in the high-temperature range, a weakly bound form of N_2 appears on the surface with decrease in temperature, and determines the nature of the desorption and exchange in this range.

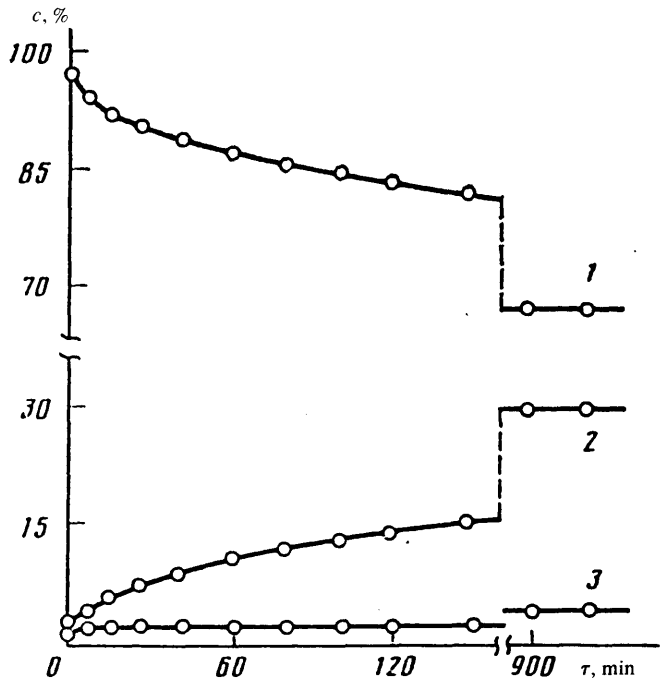

Figure 6. Dependence of the concentration c of the isotopic forms of the nitrogen molecules in the gas phase on the duration of exchange on $BaN_{0.62}$ (333 K, 52 Pa): *1*) $^{15}N^{15}N$, *2*) $^{14}N^{14}N$, *3*) $^{14}N^{15}N$.

To investigate the nature of the weakly bound form, the hetero-exchange of nitrogen on barium nitride was studied at 373 K and 333 K.[62] The kinetics of the process at 333 K are shown in Fig.6. Only a change in the concentration of the molecules $^{14}N^{14}N$ and $^{15}N^{15}N$ is observed, and there is practically no formation of mixed molecules $^{14}N^{15}N$. Thus only the reversible transfer of molecules between the surface and the gas phase takes place in the system, leading to hetero-exchange, and there is no redistribution of the atoms between the nitrogen molecules. This indicates that the low-temperature form of nitrogen is molecular in character, and also that it is inert with respect to homo-exchange.

A similar picture is observed for strontium nitride, where molecular nitrogen may be present in unexpectedly large quantities. Fig.7 gives the temperature dependence of the concentration of nitrogen in an Sr_2N specimen.[72] It can be seen that in the range 623–423 K, the concentration of nitrogen changes comparatively little, but with subsequent decrease in temperature, an abrupt change takes place, and N_2 is adsorbed in quantities corresponding to 20 surface monolayers, or ~13% of the initial concentration of nitrogen in the specimen. Experiments on the adsorption of a mixture of $^{14}N^{14}N$ and $^{15}N^{15}N$ molecules showed that all the nitrogen absorbed at a temperature below 423 K is in the molecular form and can be desorbed into the gas phase without change in the isotopic composition.

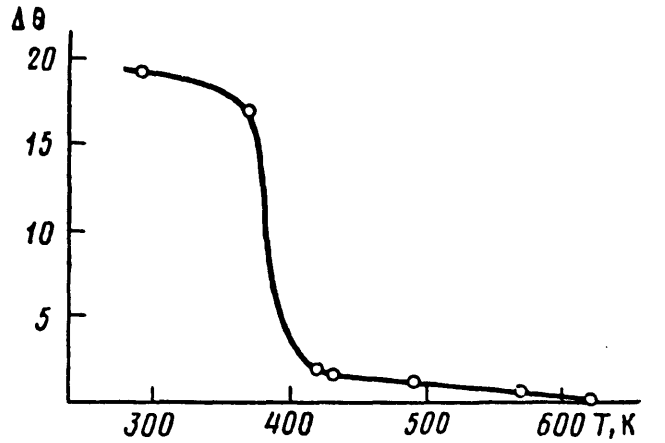

Figure 7. Change in the nitrogen concentration ($\Delta\theta$, number of monolayers) in Sr_2N with change in temperature at a pressure of 52 Pa.

This raises the question of the state of the bound nitrogen molecules. In this case it is clearly impossible to speak of physical adsorption, which is observed on many metals close to 100 K.[73] In this case there is evidently a more extensive chemical interaction. It may be assumed that in the general case, nitrogen passes through all oxidation states from 0 to −3 in the course of the reaction. If it is assumed that two-electron transitions takes place, intermediate compounds corresponding to the formal valence states N_2^0, N_2^{2-}, N_2^{4-}, and N^{3-} should be formed.[72] The nitrogen molecule shows an important feature which distinguishes it from other unsaturated compounds: in the rupture of the triple bond N ≡ N, the greater part of the energy is used up in the rupture of the first bond (527 kJ mole^{-1}); 260 kJ mole^{-1} is used up in the rupture of the second bond, and only 159 kJ mole^{-1} in the rupture of the third. This makes preferable the many-electron reduction of N_2 with the transfer of four or six electrons to the nitrogen molecule.[75] Thus the reaction with metals usually finishes with the complete rupture of the N ≡ N bond and the formation of nitrides, which can be regarded as derivatives of ammonia.

In some cases, however, mainly for alkaline earth metal nitrides, the reaction with nitrogen may lead to the formation of pernitrides.[76] The unusual features of these compounds is that a certain proportion of the nitrogen present preserves a nitrogen–nitrogen bond, so that hydrolysis gives not only NH_3 but also hydrazine, indicating according to the authors of Ref.74, that pernitrides contain nitrogen as the ion N_2^{4-}.

Interesting results have been obtained in extensive studies to find methods for the low-temperature activation of nitrogen in metal complexes in solution.[75,77] Contrary to existing ideas, it was found that complexes containing N_2 as ligand in the coordination sphere of the metal are encountered extremely widely. Moreover, it was possible to obtain catalytic systems based on Ti[77] and Mo,[75] capable of bringing about the catalytic fixation of nitrogen.

In many cases, however, the molecular nitrogen in the coordination compounds is in the inactive state, and attempts to involve it in any chemical reaction lead to the liberation of free N_2. It was of interest to determine whether the nitrogen absorbed in molecular form by strontium and barium nitrides is reactive. It was noted above that this form is not active in homomolecular exchange. It is also incapable of reacting with hydrogen. The introduction of H_2 into the system leads to the absorption of hydrogen and the displacement of nitrogen in the molecular form into the gas phase without the formation of even traces of NH_3.

Hydrolysis is widely used to study the reactivity of nitrogen in coordination compounds. This reaction has been used to test two series of strontium nitride specimens· the specimens of series *A*, containing molecular nitrogen in quantities corresponding to ~20 monolayers, and the specimens of series *B*, obtained from series *A* after desorption of the molecular form.[72] The hydrolysis was carried out using an oxidising agent (ammonium vanadate), which is incapable of reacting with NH_3 but which readily reacts with stronger reducing agents, for example hydrazine.

Table 4. Hydrolysis of strontium nitride.

Specimens	10^6 [N_2], mole g^{-1}	10^6 W_O, mole g^{-1}	10^6 W_B, mole g^{-1}	
			N_2H_4	N_2H_2
Series *A*	330	680	170	340
Series *B*	~0	20	6	12

Symbols: [N_2] is the concentration of the molecular form of nitrogen in the specimen; W_O the consumption of the oxidising agent; and W_B the concentration of the reducing agent in the hydrogenolysis products, calculated as hydrazine and di-imide.

The averaged results of the experiments are given in Table 4, and show that the consumption of the oxidising agent is determined practically completely by the presence of molecular nitrogen in the specimens. If it is assumed that the direct product of the hydrolysis is hydrazine, the calculations show that the quantity of N_2H_4 liberated corresponds to only half of the nitrogen combined in the molecular form. This gives grounds for assuming that the hydrogenolysis is undergone by a derivative of not hydrazine but di-imide, in which a double bond N=N is preserved. The protonation of this compound should give N_2H_2, whose reducing equivalent is half that of N_2H_4. With this assumption, the observed consumption of the oxidising agent corresponds satisfactorily to the concentration of molecular nitrogen in the specimens.

Thus the molecular form of nitrogen detected on strontium and barium nitrides, although insufficiently activated to react with H_2 or to take part in homomolecular exchange, is capable of being converted into the combined state as a result of the hydrolysis of the nitrides. It may be assumed that the nitrogen in this form is present as the N_2^{2-} group, analogous to the peroxide group O_2^{2-} in oxygen-containing compounds. Some of these oxygen-containing compounds also decompose with the liberation of molecular oxygen without rupture of the peroxide bond.[78]

The possible formation of derivatives of di-imide in the reaction of metal complexes with nitrogen was discussed in Ref. 75.

VI. THE HEAT OF ADSORPTION OF NITROGEN AND THE ACTIVATION ENERGY OF THE ISOTOPIC EXCHANGE OF N_2

In the isotopic exchange of oxygen on oxides, taking place by the third type of mechanism, the magnitude of the activation energy coincides satisfactorily with the heat of adsorption of oxygen.[28] Since the isotopic exchange of nitrogen also takes place by the third type of mechanism, it was of interest to determine whether the same regular feature applies to nitrogen.

The heats of adsorption of nitrogen on nitrides have been measured by two methods:[79] the calorimetric method and the kinetic isotopic method proposed in Ref. 63. The essential features of the last method are as follows. In the measurement of the rates of adsorption w_{ads} and desorption w_{des}, the observed change in pressure in the gas phase is determined by the difference between w_{ads} and w_{des}. Thus the rates are usually measured either under conditions of adsorption equilibrium, when $w_{ads} = w_{des}$ (the isotopic exchange method), or, on the contrary, at a distance from equilibrium, when one of these quantities is negligible compared with the other. In a system in which exchange is taking place by the third type of mechanism, these two processes can be distinguished using isotopes, by arranging the experiment in such a way that at the initial moment of time the adsorption flux is represented by one isotope, and the desorption flux by the other. In this case the adsorption and desorption can be measured independently while they take place simultaneously both under equilibrium conditions and at a certain distance from equilibrium. By changing the temperature for a fixed degree of covering of the surface, it is possible to determine the activation energy of adsorption and desorption, and hence the heat, which is denoted q_{kin} to distinguish it from the quantity q_{cal} determined calorimetrically. Table 5 shows that the two methods give similar results.[79]

Table 5. The heat of adsorption and the activation energy of the isotopic exchange of nitrogen.[79]

Nitride	Sr_2N	$BaN_{0.62}$	CeN	$UN_{1.70}$	α-U_2N_3
q_{cal}, kJ $mole^{-1}$	60	115	125	170	240
q_{kin}, kJ $mole^{-1}$	60	90—140	—	—	225
$E(N_2)$, kJ $mole^{-1}$	55	50	130	105	225

Comparison of the activation energy of isotopic exchange $E(N_2)$ with the heat of adsorption of nitrogen (Table 5) showed that the values agree satisfactorily for strontium and cerium nitrides and α-U_2N_3. $BaN_{0.62}$ and $UN_{1.70}$, however, show an appreciable discrepancy, which was attributed[79] to the partial binding of nitrogen by bulk layers of the nitride.

Barium nitride and the uranium nitride $UN_{1.70}$ can readily undergo a change in chemical composition with change in the conditions. Since in the measurement of the heat of adsorption, a pressure higher than the equilibrium pressure is established at the initial moment, it is natural to expect that this may lead not only to the adsorption of nitrogen on the surface but also to its transfer from the surface into the bulk, which corresponds to two processes:

$$N_2 + 2[\ ]_s \rightarrow 2[N]_s + q_s \quad (8)$$

$$N_2 + 2[\ ]_v \rightarrow 2[N]_v + q_v \quad (9)$$

Here, $[\ ]_S$ and $[\ ]_V$ represent unoccupied positions on the surface and in the volume respectively. In this case the measured heat is

$$q_{meas} = \frac{n_s}{n} q_s + \frac{n_v}{n} q_v$$

where n_S and n_V are the numbers of molecules transferred from the gas phase to the surface and to the volume respectively; $n = n_S + n_V$. When $q_V > q_S$, this leads to a value of q_{meas} which is higher than the heat of adsorption q_S. Similarly, the redistribution of nitrogen between the surface and the volume also leads to distortion of the true value of the heat of adsorption when the kinetic method is used.

In some cases, the process of volume binding according to Eqn.(9) may predominate, as is probably the case for $BaN_{0.62}$ and $UN_{1.70}$. In the equilibrium diagram, uranium nitride $UN_{1.70}$ lies in the range of compounds of variable composition bounded by the phases U_2N_3 and UN_2. The heat of adsorption of nitrogen on this specimen (170 kJ mole^{-1}) is close to the heat of the reaction

$$UN_{1.51} + 0.09\,N_2 \rightarrow UN_{1.69}$$

which amounts to 185 kJ mole^{-1}.[80] The heat of adsorption of nitrogen on barium nitride (115 kJ mole^{-1}) also does not differ greatly from the heat of the process

$$6Ba_3N + N_2 \rightarrow 4Ba_3N_2$$

which equals 140 kJ mole^{-1}.[55]

The influence of bulk processes has also been noted in the measurement of the heats of adsorption of oxygen on various oxides.[81] Since oxides have an extremely stable chemical composition and a comparatively low oxygen mobility, however, this does not lead to significant discrepancies between the values of $E(O_2)$ and $q(O_2)$. Distortion of the values obtained for the heat of adsorption may also take place in the case of metallic catalysts, because of solution processes in the layers of metal next to the surface. It must therefore be borne in mind that the measured value of the heat of adsorption may not always characterise the bond energy of the surface species taking part in the catalytic process.

Unlike the heat of adsorption, the activation energy of isotopic exchange is measured under conditions of adsorption equilibrium. In this case, therefore, there are no secondary processes leading to the values of q which are too high. Thus Table 5 shows that the discrepancy (where it exists) is observed only in the direction of an increase in q above E. The activation energy of isotopic exchange apparently corresponds to the true value of the heat of adsorption. For systems with a labile chemical composition, isotopic exchange probably provides the most reliable method for determining it.

VII. THE DEPENDENCE OF THE CATALYTIC ACTIVITY IN ISOTOPIC EXCHANGE REACTIONS ON THE HEATS OF ADSORPTION OF NITROGEN AND OXYGEN

Table 3 shows that the rate of the isotopic exchange of nitrogen on different catalysts differs by many powers of ten. It cannot be related to any physicochemical characteristics of the catalysts. As in the case of oxides, it may be assumed that the bond energy of the surface nitrogen should be of the greatest interest from this viewpoint. Thus Fig.8, constructed from the data in Table 3, shows a distinct relationship between the catalytic activity and the heat of adsorption $q(N_2)$, for which the value of $E(N_2)$ was used.

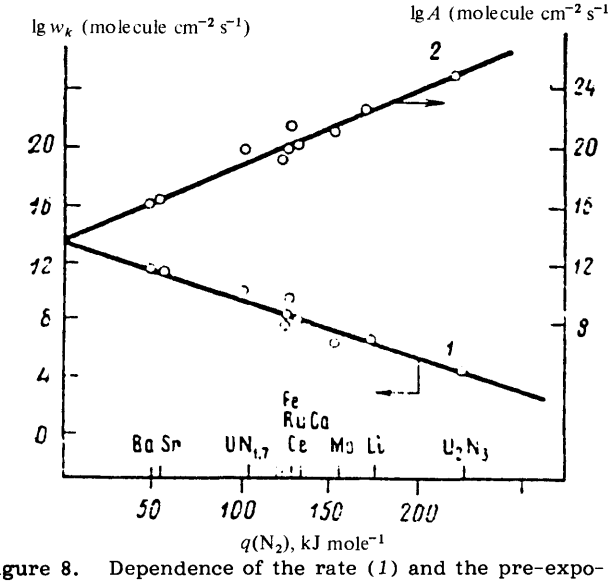

Figure 8. Dependence of the rate (*1*) and the pre-exponential factor (*2*) of the isotopic exchange of N_2 on nitrides and metallic iron and ruthenium (573 K, 52 Pa) on the heat of adsorption.

The highest activity in the isotopic exchange of nitrogen is shown by strontium and barium nitrides, which have the minimum heat of adsorption, equal to ~50 kJ mole^{-1}. The rate of exchange of nitrogen on these catalysts is one hundred times the rate of exchange on Fe. The lowest activity is shown by α-U_2N_3, on which the heat of adsorption of nitrogen is 225 kJ mole^{-1}. Overall, an increase in the heat of adsorption by 175 kJ mole^{-1} in the series of nitrides and metals examined leads to a decrease in the rate of exchange by a factor of 10^7. There is a simultaneous increase in the pre-exponential factor, corresponding to the existence of a compensation effect.

The heat of adsorption of nitrogen on magnesium nitride is probably even higher than that on α-U_2N_3, and this specimen does not show appreciable activity up to 973 K.[25]

A similar relationship is observed for the isotopic exchange of oxygen on oxides, as can be seen by comparing Fig.8 and Fig.3. Moreover, this similarity is not only qualitative, but also quantitative, as can be clearly seen from Fig.9, which gives simultaneously the dependence of the isotopic exchange of nitrogen and the isotopic exchange of oxygen, carried out

under identical conditions, on the corresponding values of the heats of adsorption. The fact that the relationships coincide is extremely unexpected, and indicates that the chemical nature of the reacting molecules and the chemical nature of the catalysts are important primarily in the way in which they influence the heat of reaction. If the heats are equal, the rates of exchange are approximately the same, irrespective of whether the system contains molecular nitrogen or oxygen.

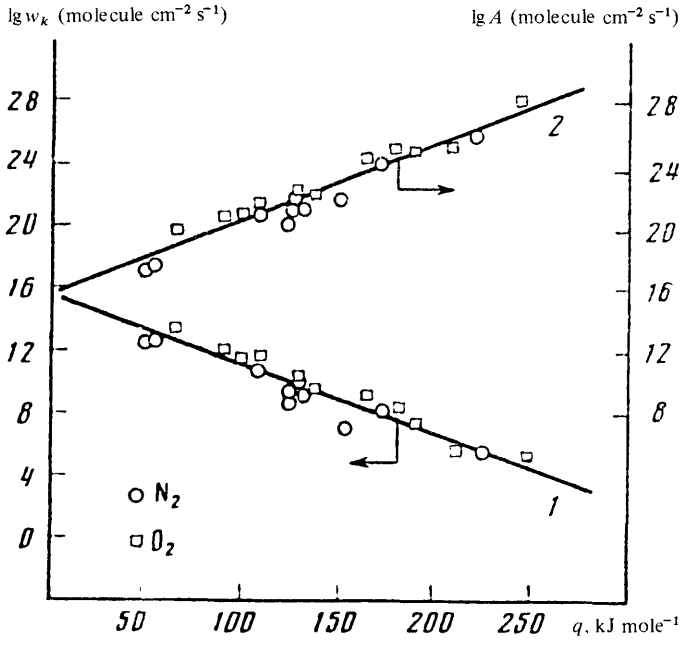

Figure 9. Dependence of the rate (*1*) and the pre-exponential factor (*2*) of the isotopic exchange of nitrogen and oxygen (573 K, 1.33 kPa) on the heat of adsorption.

The similarity in the entropy factors is probably because the entropies of the free molecules of nitrogen and oxygen are similar and the exchange mechanisms are the same. It is more difficult to understand why the values of the activation energy of isotopic exchange of nitrogen and oxygen are equal with identical values of q, since in the case of N_2 the reaction at each stage involves bonds whose energy is 450 kJ mole^{-1} greater than for O_2. The only explanation for this fact is probably that in the dissociative adsorption of both N_2 and O_2 there is almost complete compensation of the energy required for rupture of the bonds in these molecules, by the energy of the reaction of the resulting atoms with the surface. In other words, the heat of adsorption makes the principal contribution to the energy barrier of the equilibrium adsorption–desorption process.[82]

There are a number of facts which show an analogy between the observed regularity and the energy characteristics of more complex catalytic reactions. Thus in Ref. 83 it is the heat of the process that is used to characterise the reactivity of the substances being oxidised, and its use makes it possible to describe satisfactorily the regular features of the complete oxidation.

Of considerable interest is the numerical value of the coefficient α in Eqn.(3), which shows the fraction of the heat of adsorption of oxygen $q(O_2)$ appearing in the activation energy of the oxidative reaction. Since in different reactions the removal of oxygen takes place in different activated complexes, the coefficient α should apparently change with variation of the chemical character of the reacting molecules. Analysis of a large number of oxidative reactions has shown, however, that the value of α remains approximately constant and equal to ~0.5 in all cases.[83] This coefficient is also equal to ~0.5 for a number of other reactions, including the reaction of ammonia synthesis.[85] The coefficient α has also been found to be constant in the isotopic exchange of nitrogen and oxygen, in spite of the difference in the chemical character of the O_2 and N_2 molecules, the only difference being that the coefficient α in both cases is equal to 1, since the quantities E and q are equal.

Finally, to return to the fact that the relationships for nitrogen and oxygen in Fig. 9 are identical, it should be noted that the rate of exchange, in addition to the heat of adsorption, is also determined by the proportion of the active surface. Thus if the surfaces of the catalysts being studied are biographically non-uniform, the non-uniformity cannot be strongly defined. Otherwise, it would be necessary to assume the existence of some universal law of distribution of the active centres of the surface with respect to energy for all the catalysts which have been compared.

VIII. ESTIMATION OF THE RATE OF THE SYNTHESIS OF AMMONIA FROM DATA ON THE ISOTOPIC EXCHANGE OF N_2

The present section considers first those predictions about the synthesis of ammonia that can be made using data on the exchange of nitrogen. It has been noted that in the limiting stages of oxidation reactions, the removal of oxygen from a catalyst surface takes place via different activated complexes, which, in addition to oxygen, also contain various fragments of the substance being oxidised. Naturally, these complexes are not formed in isotopic exchange. Thus from the rate of exchange of O_2 it is possible to predict only the relative change in the rates of oxidation in a given series of catalysts. The synthesis of ammonia under conditions not too far removed from equilibrium, however, takes place by the Temkin–Pyzhov mechanism, whose limiting stage is the adsorption of nitrogen, that is a stage which is present in "pure form" in isotopic exchange. In this case, exchange data make it possible to calculate not only the relative values but also the absolute values of the rates of synthesis.[22,86]

The equation for calculating the rate of the synthesis of ammonia has the following form:[22]

$$w_c = w_k(p/p^* - 1) \qquad (10)$$

where w_c is the rate of the synthesis of ammonia, measured at a partial pressure of nitrogen in the reaction mixture p; p^* is the volatility of the nitrogen adsorbed on the catalyst under the conditions of the synthesis reaction; and w_k the rate of the isotopic exchange of N_2 at a nitrogen pressure equal to p^*. The value of p^* is calculated from the equation

$$p^* = \frac{1}{K_p}\frac{p^2(NH_3)}{p^3(H_2)}$$

where $p(NH_3)$ and $p(H_2)$ are the partial pressures of ammonia and hydrogen respectively in the reaction mixture, and K_p the equilibrium constant of the reaction

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

Thus Eqn.(10) shows that the activity of the catalysts in the

synthesis of ammonia should be proportional to their activity in isotopic exchange, measured under identical conditions.

Some data on the activity of nitrides in the synthesis of NH_3 [25,53,61,66] are given in Table 6, which also gives for comparison the data for the promoted iron catalyst SA-1.[61] It can be seen that Mg nitride, which is inert in the isotopic exchange of nitrogen, is also inactive in the synthesis of ammonia. The lanthanides, except for cerium, have a low activity in exchange, and show appreciable activity in the synthesis only in the temperature range close to 800 K, whereas CeN and $UN_{1.70}$ are active in both reactions. Even a qualitative examination shows, however, that in most cases, particularly on the nitrides of Sr and Ba, which are of greatest interest (the expected rate of synthesis should be 100–1000 times that on Fe), the experimentally measured rate is found to be much lower than that calculated from data on the isotopic exchange of nitrogen using Eqn.(10), or even close to zero.

Table 6. The activity of nitrides in the synthesis of ammonia at a pressure of 98 kPa.

Nitride	T, K	$[NH_3]$, mole %	lg w (molecule $cm^{-2}s^{-1}$)		Phase composition after the synthesis
			expt	calc	
Cu_3N	423	2.2	13.0	0.0	metal
Li_3N	673	0.03	11.3	12.0	hydride
$MgN_{0.6}$*	873	—	—	—	nitride
$CaN_{0.8}$	773	0.08	12.3	13.3	mixed phase
$SrN_{0.5}$*	873	—	—	—	mixed phase
$BaN_{0.62}$	573	0.32	13.8	14.5	hydride
LaN	773	0.054	11.2	—	nitride
CeN	673	0.26	11.4	11.5	nitride
PrN	773	0.075	10.8	—	nitride
NdN	773	0.054	10.3	—	nitride
TbN	823	0.025	10.3	—	nitride
HoN	773	0.030	10.8	—	nitride
$UN_{1.70}$	623	0.24	11.6	12.9	nitride
CA-1	673	0.27	11.8	—	

*Inactive

The discrepancy may be due to two factors: either the reaction does not take place by the Temkin–Pyzhov mechanism, so that the assumptions on which the calculation is based are incorrect, or side reactions take place under the synthesis conditions, leading to a decrease in the rate of the catalytic reaction. Subsequent studies have shown[66] that the factor responsible lies not in a change in the mechanism but in the physicochemical characteristics of the nitrides, which are examined below.

IX. THE STABILITY OF NITRIDES. THERMODYNAMIC ESTIMATIONS

The study of the synthesis of ammonia has revealed extremely significant differences in the behaviour of nitrides. Some nitrides, including those of the lanthanides and uranium, have been found to be stable in a nitrogen–hydrogen mixture;[66] in this case the formation of ammonia is the result of a catalytic process. X-Ray diffraction data have shown that the phase composition of the original catalysts remains unchanged after the reaction (Table 6). The nitrides of another group, namely those of lithium and the alkaline earth metals, are unstable and undergo phase transformations during testing. In this case, the formation of ammonia is also observed under the conditions of the experiment, but this results not from a catalytic process but from a chemical reaction between the nitride and the hydrogen of the gas phase. The formation of ammonia stops completely after the nitride has been converted into the hydride.

The ability to form hydrides is well known for the electropositive metals of groups I, II, and III of the periodic system.[87] To understand the characteristic features of the behaviour of nitrides and to determine the possible range of their stable operation, it is appropriate to examine the thermodynamic properties from the viewpoint of the stability of the nitrides in a nitrogen–hydrogen mixture.

It will be assumed that the original system contains either a nitride phase, for example M_3N, or the corresponding hydride phase MH. It will be assumed that the nitrogen pressure is 25 kPa, and the hydrogen pressure 75 kPa. To estimate the stability of a given phase, it is necessary to determine the free energy of the reaction:

$$6MH + N_2 \rightarrow 2M_3N + 3H_2 \qquad (11)$$

Since the change in the heat capacity in this reaction is slight, it will be assumed that

$$\Delta G^0_T = \Delta H^0_{298} - T\Delta S^0_{298}$$

In addition to reaction (11), the formation of NH_3 is also possible in the system being considered. Since the free energy of formation of ammonia is extremely small, however, this possibility will not be taken into account, since the calculations are only approximate.

Table 7. Stability of nitrides in a nitrogen–hydrogen mixture.

Compound	$-\Delta H^0_{f,298}$, kJ $mole^{-1}$	$-\Delta S^0_f$, J $mole^{-1}$ K^{-1}	Stability range
Li_3N	197	79	>600 K
LiH	91	69	—
Mg_3N_2	462	202	unlimited
MgH_2	75	127	—
Ca_3N_2	440	210	>700 K
CaH_2	189	131	—
Sr_3N_2	391	225	>600 K
SrH_2	177	158	—
Ba_3N_2	364	243	>800 K
BaH_2	179	156	—
CeN	327	107	unlimited
CeH_2	253	181	—
U_2N_3	374	334	unlimited
UH_3	117	186	—

Table 7 gives the original thermodynamic data, taken from Ref.87–91, and the results of an estimation by the present authors of the temperature range of stability of the nitrides. In agreement with experimental observations of the phase composition of the specimens after the experiments (Table 6), the calculation showed that the nitrides of the lanthanides and uranium are stable throughout the entire temperature range. According to the calculation, the nitrides of lithium and the alkaline earth metals should be stable only at temperatures above 600–800 K, and that their hydrides are stable at lower temperatures. In fact, the situation for the nitrides of lithium and the alkaline earth metals is found to be even less favourable. Thus in the presence of H_2 these systems can also form mixed compounds containing nitrogen and hydrogen (amides and imides), whose existence cannot be taken into account, since their thermodynamic properties are unknown. As a result of the existence of these compounds, the range of stability of the nitrides of the metals of groups I and II is displaced to much higher temperatures, which are of no interest for catalysis, because of the low equilibrium yields of NH_3.

The catalytic activity of the actual mixed phases is low. Thus in the presence of the mixed phase formed by strontium, the formation of ammonia is not observed up to 873 K.[92]

In the case of the unstable nitrides, hydrogen also has a strong and irreversible deactivating influence on the isotopic exchange of N_2.[25]

An interesting representative of the group of unstable nitrides is barium nitride, for which the conversion into the hydride takes place particularly readily, leading to a high rate of formation of ammonia in the low-temperature range (470–570 K). The reaction of barium nitride with H_2 takes place in two stages.[92] In the first stage, after the introduction of the nitrogen–hydrogen mixture, vigorous absorption of H_2 takes place without the liberation of ammonia, and is complete with the formation of the compound $BaN_{0.6}H_{1.8}$. This overall composition probably corresponds not to any individual substance but to a mixture of nitrogen- and hydrogen-containing compounds.

In the second stage, hydrogenation takes place with the liberation of NH_3. The total quantity of ammonia formed corresponds closely to the initial concentration of nitrogen in the nitride, and is independent of whether the nitrogen–hydrogen mixture of pure H_2 is passed over the specimen. This indicates that the nitrogen of the gas phase is not involved in the catalysis process, and that NH_3 is formed only as a result of the hydrogenation of the nitride.

Barium hydride can be reconverted into the nitride by heating in an atmosphere of nitrogen, to give a cyclic process for preparing ammonia.[92]

Unlike other metals, copper cannot form hydrides. The nitride Cu_3N is thermodynamically unstable ($\Delta H^0_{f\ 298} = 75$ kJ mole^{-1}), which, like the nitrides of Fe[45] and Ge,[43] readily decomposes in the presence of hydrogen to give metallic copper and an equivalent quantity of ammonia.

X. COMPARISON OF THE EXPERIMENTAL AND CALCULATED RATES OF SYNTHESIS OF AMMONIA

The calculation of the rate of synthesis of NH_3 from isotopic exchange data is obviously meaningful only for stable nitrides. Table 6 shows that the highest activity corresponds to uranium nitride, on which the rate of ammonia synthesis is close to the rate of the same process on an iron catalyst. A high activity is also shown by cerium nitride, and this has stimulated the examination of a fairly large number of lanthanides in order to find in this series other catalysts capable of bringing about the synthesis of ammonia at a high rate. However, in this reaction as in isotopic exchange, the activity of all the other nitrides was found to be lower by several powers of ten than that of CeN.

This result is extremely unexpected, since the lanthanide nitrides have the same crystal structure and similar thermodynamic and chemical properties. The difference must be attributed to differences in the electrical characteristics, since CeN has the highest electrical conductivity of nitrides in this series.[54] An interesting feature is that a similar regularity is also observed in the series of lanthanide oxides, where the maximum electrical conductivity and the maximum activity in the oxidation of hydrogen correspond to the element next to cerium, namely praseodymium.[30]

The calculated and experimental rates of ammonia synthesis are compared in Fig.10, taken from Ref.53. The broken straight line corresponds to the equality $w_{calc} = w_{expt}$. (It should be noted that Fig.10 cannot be used to reach conclusions about the relative activity of catalysts, since the data for different catalysts relate to different conditions.) It can be seen that for the nitrides of cerium and molybdenum and for metallic iron, there is satisfactory agreement between the calculated and measured rates, whereas for uranium nitride a considerable discrepancy is observed, and w_{expt} is smaller than w_{calc} by a factor of more than 10.

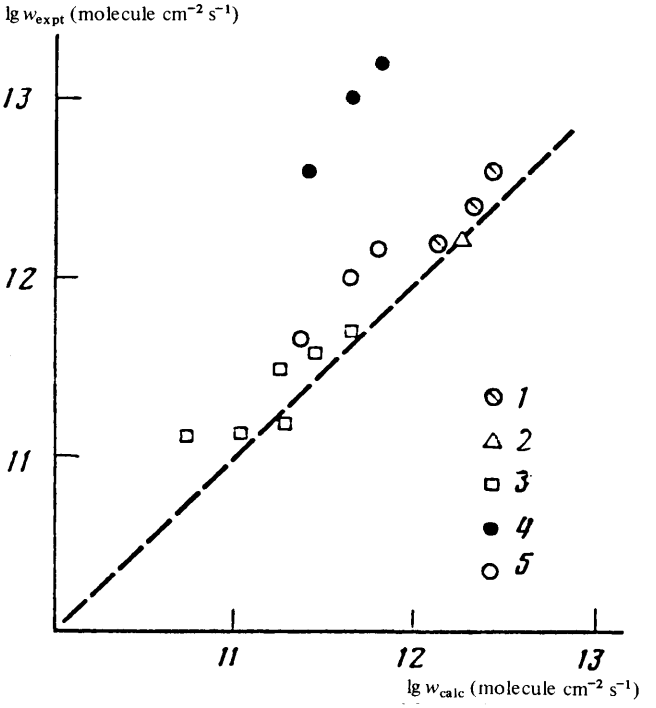

Figure 10. Comparison of the experimental and calculated rates of ammonia synthesis on Fe (*1*), Mo_2N (*2*), CeN (*3*) and on $UN_{1.70}$ without allowance (*4*) and with allowance (*5*) for the influence of H_2.

It is natural to assume that the fact that the rate of ammonia synthesis is lower than the calculated value in this case may be due to the deactivating influence of hydrogen, although the presence of hydrogen cannot bring about phase transformations in uranium nitride. This was confirmed in a study of the influence of H_2 on the isotopic exchange of nitrogen.[53] The introduction of hydrogen into the system leads to its appreciable absorption and is accompanied by a decrease in the rate of the isotopic exchange of N_2. The retardation by hydrogen in this case is reversible, and when the exchange is subsequently carried out in pure nitrogen, the activity is completely restored. The theoretical calculation of the rate of ammonia synthesis on uranium nitride with allowance for the influence of hydrogen on the activation of N_2 [53] leads to satisfactory agreement with experiment (Fig.10).

Hydrogen has no deactivating action and has no influence on the isotopic exchange of nitrogen on a cerium nitride catalyst.[24]

Thus for nitrides, as for metallic catalysts, where the deactivating action of hydrogen has no significant influence or can be taken into account, the isotopic exchange of N_2

provides an adequate characteristic of the activation of molecular nitrogen and its ability to take part in the ammonia synthesis reaction.

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The results examined in the present review show the general character of the mechanism and regular features of the catalytic action of oxides in the activation of molecular oxygen and extensive oxidation reactions on the one hand, and the catalytic action of metals and nitrides in the activation of molecular nitrogen and the synthesis of ammonia on the other. This makes it possible to approach from a single viewpoint the problem of selecting catalysts for the range of reactions being considered.

It is not excluded that this general character may be even wider and may be observed in other systems, where the activation of a diatomic molecule takes place by dissociative adsorption on a catalyst surface. It is therefore of interest to carry out comparative studies of a number of analogous systems, and in particular to compare the catalytic action of hydrides in the isotopic exchange of H_2 and hydrogenation, and of chlorides in the isotopic exchange of Cl_2 and chlorination.

It may also be noted that the activation of nitrogen, that is a molecule which is often placed in a unique position because of its inertness, is in fact not an exceptional phenomenon. It obeys the same regular features as the activation of molecular oxygen.

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The Coupled Reactions of Oxidation by Hydrogen Peroxide

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The results of basic studies of chemical coupling in the gas-phase oxidation of various substrates by hydrogen peroxide have been analysed. The general characteristics of the mechanism of chemical coupling in gas-phase and liquid-phase oxidation by hydrogen peroxide have been examined.
The bibliography contains 81 references.

CONTENTS

I. Introduction 974
II. Chemical coupling in gas-phase oxidation by hydrogen peroxide 974
III. Chemical coupling in liquid-phase oxidation by hydrogen peroxide 982
IV. The ability of hydrogen peroxide to induce oxidation, and possible new applications 983

I. INTRODUCTION

Many reactions of practical importance involving the direct oxidation of various substrates by molecular oxygen do not correspond to present-day requirements, since practically all existing technical processes take place with a low selectivity.

In the development of present-day oxidation processes in chemical technology, the use of chemically combined forms of oxygen (O_3, H_2O_2, ROOH, etc.) and the principles of coupled processes are acquiring increasing importance.

Interest in the study of oxidation in coupled chain reactions has increased considerably as a result of the work of Academician N.M.Emanuel' and his school,[1,2] who were the first to formulate the concept of radical forms of coupled chemical reactions: "...the radicals generated by one of the reactions taking place in the system act as active reagents for another reaction which does not occur to a significant extent by itself under these conditions".

This statement forms the basis of the mechanism of the coupled oxidation of various substrates by hydrogen peroxide.

The present review examines reactions involving coupled oxidation by hydrogen peroxide, in which it has been shown that H_2O_2 can be used effectively both to discover new chemical reactions and to intensify and simplify the technology of oxidation processes of practical importance.

Hydrogen peroxide has various applications, and its world production has been estimated as several hundred thousand tons.

The use of H_2O_2 in industry in most cases has led to an improvement in the quality of production, a decrease in its cost, a decrease in environmental pollution, and increase in productivity, simplification of the technology, etc.

Because of its intermediate position in the redox triad

$$O_2 \underset{-2H}{\overset{2H}{\rightleftarrows}} H_2O_2 \underset{-2H}{\overset{2H}{\rightleftarrows}} H_2O$$

H_2O_2 shows a dual reactivity, and can act as an electron donor or as an electron acceptor, depending on the nature of the substrate.

Studies of reactions involving H_2O_2 have dealt chiefly with methods of preparation, the mechanism of the homogeneous and heterogeneous decomposition of H_2O_2, and the use of H_2O_2 as polymerisation initiator and as oxidising agent for the liquid-phase oxidation of organic substrates using transition metal compounds or enzymes as catalysts. Until recently there were practically no published data on the use of H_2O_2 as an oxidising agent in the gas phase.

II. CHEMICAL COUPLING IN GAS-PHASE OXIDATION BY HYDROGEN PEROXIDE

The use of hydrogen peroxide as an oxidising agent in the gas phase (as shown below) makes it possible to oxidise effectively aromatic compounds, alcohols, halogen-containing compounds,[3] and even nitrogen.[4] It is assumed that the oxidation is due to the existence of chemical coupling.[5,6] The primary reaction in this case is

$$H_2O_2 + H_2O_2 \rightarrow \underset{\text{intermediates}}{[\dot{O}H,\ H\dot{O}_2]} \rightarrow 2H_2O + O_2 \quad \Delta G^{\circ}_{298} = -58.8 \text{ kcal mole}^{-1} \qquad (1)$$

The $HO_2^{\bullet}$ free radicals formed in this reaction bring about the oxidation of the substrate according to the overall equation

$$H_2O_2 + \text{acceptor} \rightarrow \text{reaction products} . \qquad (2)$$

In the H_2O_2–acceptor–H_2O system, hydrogen peroxide is converted into the active form as the radical $HO_2^{\bullet}$ (in which the acceptor–donor properties of H_2O_2 are preserved), which transfers the inductive action of the primary reaction to the secondary reaction. The $HO_2^{\bullet}$ radical acts as it were as the intermediary agent between the coupled reactions, and the "active oxygen" in it is responsible for the selective oxidation.[6]

1. The Coupled Dehydrogenation of Various Substrates by Hydrogen Peroxide

Experimental studies to detect chemical coupling in gas-phase oxidation by hydrogen peroxide[6,7] were carried out in a flow system using an integral reaction vessel (ideal displacement conditions), whose design made it possible to introduce H_2O_2 into the reaction zone.

To determine which species is responsible for oxidation in the RH–H_2O_2–H_2O system, the model system chosen was the coupled dehydrogenation of ethylbenzene by a 15% aqueous solution of hydrogen peroxide and by molecular oxygen. For comparison of the results, the O_2 was supplied in quantities equivalent to its concentration in 15% aqueous H_2O_2 solution.[7,8]

Experiments on the coupled dehydrogenation of ethylbenzene (ETB) in the range 580–620 °C showed that the use of hydrogen peroxide gives high yields of styrene, equal to 39.3 mass % and 90 mass %, calculated respectively for the initial ETB and the ETB reacted, at 620 °C. At the end of the reaction, no condensation products (CP) were detected, and the volatile products consisted chiefly of CO_2, in quantities not exceeding 1% by weight.

In the dehydrogenation of ethylbenzene by molecular oxygen, the yields of styrene are much lower (8–10 mass %) than in the first case, and condensation products are formed in quantities of up to 1.7% by wt. on the walls of the quartz reaction vessel. In addition, the quantity of O_2 in the gaseous products reaches 80 % by volume, whereas the gaseous products of the conjugated dehydrogenation by hydrogen peroxide do not contain molecular oxygen. Thus the dehydrogenating agent in the system is hydrogen peroxide, that is the coupled dehydrogenation by hydrogen peroxide takes place by a mechanism which differs fundamentally from that of high-temperature oxidation by molecular oxygen. Although by itself the formation of an oxygen atom by the decomposition of H_2O_2 in a hydrocarbon medium by a heterogeneous process is unlikely, nevertheless to eliminate the possibility of the participation of the atoms of O_2 in the dehydrogenation, the decomposition of nitrous oxide was used as a source of oxygen atoms: [9]

$$N_2O \rightarrow N_2 + O^{\cdot}$$

The degree of decomposition of N_2O in the presence of butane and cyclohexane at 500–600 °C is 25 mole % and 30 mole % respectively, [10,11] indicating that the decomposition of N_2O is independent of the presence of hydrocarbons in the medium.

In addition to unsaturated compounds, a large number of side products (H_2, CH_4, C_2H_6, C_2H_4) were found in the products of the transformation of C_4H_{10}. The dehydrogenation of C_6H_{12} in the presence of H_2O_2 is also characterised by a much higher selectivity at higher degrees of conversion, compared with the reaction in the presence of N_2O, where the only active intermediate species is atomic oxygen (see Table 1). [11,23]

Table 1. The coupled dehydrogenation of cyclohexane with the participation of hydrogen peroxide and nitrous oxide. [11,23]

System	C_6H_{10}, mass %	C_6H_8, mass %	C_6H_6, mass %	Selectivity, %
$C_6H_{12}+H_2O_2$	20	4	3	88
$C_6H_{12}+N_2O$	9	2	7	80

Thus the mechanism of dehydrogenation by hydrogen peroxide differs from that of oxidative dehydrogenation by molecule oxygen and nitrous oxide. The participation of an oxygen atom as an active reaction centre in the conjugated oxidation of the substrate by hydrogen peroxide is therefore unlikely, and elementary reactions involving it need not be considered in the reaction mechanism. This conclusion is confirmed by a study of the dehydrogenation of butane both by hydrogen peroxide and by nitrous oxide. [10]

To establish the possibility that surfaces influence the nature of the reaction of H_2O_2 with hydrocarbons, the conjugated dehydrogenation of various alkylbenzenes was studied in reaction vessels treated with inorganic salts. [12] The results of these experiments indicate that in all cases the reaction shows an appreciable sensitivity to the nature of the surface of the reaction vessel. The yields of the desired products decrease in the order:

$$B_2O_3 > \text{untreated reaction vessel} > K_2B_4O_7 > KBr > KCl > BaBr_2$$

The results correlate with data from Ref. 13, where it was shown that a quartz surface treated with metal salts influences the rate of the destruction of $HO_2^{\cdot}$ radicals, which decreases in the same salt sequence. This indicates that the surfaces which are most active in chain termination as a result of the destruction of $HO_2^{\cdot}$ are least favourable for the conjugated dehydrogenation of hydrocarbons.

The kinetic estimation of the decomposition of H_2O_2 to $HO_2^{\cdot}$ and $^{\cdot}OH$ free radicals is of interest in this connection. The decomposition of H_2O_2 in the gas phase has been fairly well studied, and takes place by the following mechanism: [14–16]

	$\lg A$, $cm^3 mole^{-1} s^{-1}$	E, kcal $mole^{-1}$
$H_2O_2 + M \xrightarrow{k_1} 2\dot{O}H + M$	17.08	45
$H_2O_2 + \dot{O}H \xrightarrow[k_2]{} HO_2^{\cdot} + H_2O$	13.0	1.8
$HO_2^{\cdot} + \text{wall} \xrightarrow{k_3} HO_{2\,ads}$	1.0	8.2
$^{\cdot}OH + \text{wall} \rightarrow OH_{ads}$	0.3	7.0

where M is the total number of molecules in the reaction volume, and A the pre-exponential factor.

According to this scheme

$$\frac{[HO_2^{\cdot}]}{[\dot{O}H]} = \frac{k_1}{k_2}[H_2O_2] \qquad (3)$$

which makes it possible to estimate the ratio of the concentrations of the active centres in the system.

Under the conditions of the experiment, [4] the ratio (3) usually lies in the range 10^3–10^7, that is the concentration of the radical $HO_2^{\cdot}$ in the gas phase is many powers of ten greater than that of $^{\cdot}OH$.

Thus dehydrogenation in the presence of H_2O_2 evidently takes place by a free-radical mechanism, and the rate of the process is determined mainly by the concentration of $HO_2^{\cdot}$ in the system.

The mechanism of dehydrogenation by hydrogen peroxide can be illustrated by several examples.

The kinetics and yield of the products of the dehydrogenation of ETB by hydrogen peroxide [7,17] in the temperature range 500–600 °C at volume rates of supply of ethylbenzene of 0.2–0.8 h^{-1} and ratios $C_6H_5C_2H_5 : H_2O_2$ in the range from 1:1 to 1:4 depend on the ratio of the surface area (S) to the volume (V). Under optimum conditions the yield of styrene reaches 40% by weight with a selectivity of 90% by weight.

The mechanism of the process involves the following elementary stages: [17]

$$H_2O_2 \rightarrow 2\dot{O}H - 52.0 \text{ kcal mole}^{-1} \qquad (4)$$

$$H_2O_2 + \dot{O}H \rightarrow H\dot{O}_2 + H_2O + 26.7 \text{ kcal mole}^{-1} \qquad (5)$$

$$C_6H_5C_2H_5 + \dot{O}H \rightarrow C_6H_5\dot{C}_2H_4 + H_2O + 42.9 \text{ kcal mole}^{-1} \qquad (6)$$

$$C_6H_5\dot{C}_2H_4 \rightarrow C_6H_5C_2H_3 + H - 52.7 \text{ kcal mole}^{-1} \qquad (7)$$

$$C_6H_5C_2H_5 + H\dot{O}_2 \rightarrow C_6H_5\dot{C}_2H_3 + H_2O + \dot{O}H + 26.7 \text{ kcal mole}^{-1} \qquad (8)$$

$$H_2O_2 + H \rightarrow H_2O + \dot{O}H + 68.4 \text{ kcal mole}^{-1} \qquad (9)$$

$$C_6H_5C_2H_5 + HO_2^{\cdot} \rightarrow C_6H_5\dot{C}_2H_4 + H_2O_2 + 14.7 \text{ kcal mole}^{-1} \qquad (10)$$

$$HO_2^{\cdot} + \text{wall} \rightarrow HO_{2\,ads} \qquad (11)$$

$$^{\cdot}OH + \text{wall} \rightarrow OH_{ads} \qquad (12)$$

This scheme includes three paths for the chain formation of styrene in the $C_6H_5C_2H_5$–H_2O_2–H_2O system.

The hydroxyl radical formed in elementary stage (4) is consumed in the bulk phase by two possible reactions, (5) and (6). Comparison of the kinetic parameters of the elementary stages (5) and (6), whose activation energies are 1–2 kcal $mole^{-1}$ [14] and 5–8 kcal $mole^{-1}$ [18] respectively, shows that the rate of reaction (5) is much greater than that of reaction (6). Thus in the $C_6H_5C_2H_5$–H_2O_2–H_2O system, of

the two paths by which $^{\cdot}OH$ are consumed, stage (5) is more probable. A noteworthy feature is that the formation of hydrocarbon radicals by the reaction $RH + {}^{\cdot}OH \rightarrow R^{\cdot} + H_2O$ would have led, in subsequent stages of development of the process, to the formation of new free radicals $RO^{\cdot}$ and $RO_2^{\cdot}$. Their transformations should lead to the appearance of oxygen-containing substances and products of oxidative cracking in the reaction products, in addition to unsaturated compounds.[19] The products of the dehydrogenation of ethylbenzene do not include organic oxygen-containing compounds, however; at relatively low yields of styrene (about 20 mass %), products of oxidative cracking are not detected either.[7]

Thus the elementary reaction (8) is apparently the most probable.[17] Usually, the activation energy of stage (10) $E_{10} > 12.5$ kcal mole^{-1} ($\lg A_{10} = 9.4$ cm^3 mole^{-1} s^{-1}),[20] and for stage (8), E_8 does not exceed 11.0 kcal mole^{-1} ($\lg A_8 = 9.6$ cm^3 mole^{-1} s^{-1}).[17,21] For chain termination reactions by the destruction of the free radicals $^{\cdot}OH$ and $HO_2^{\cdot}$ on the walls of the quartz reaction vessel, their accommodation coefficients were determined:[13,17] $\varepsilon_{OH} = 0.5 \times 10^{-6}$ and $\varepsilon_{HO_2} = 0.2 \times 10^{-5}$.

Thus estimation of the rates of the elementary stages (4) to (12) indicates that coupled dehydrogenation is an unbranched chain reaction, in which chain propagation involves two stages:

$$H_2O_2 + \dot{O}H \xrightarrow{k_5} H\dot{O}_2 + H_2O \qquad (5)$$

$$C_6H_5C_2H_5 + H\dot{O}_2 \xrightarrow{k_8} C_6H_5\dot{C}_2H_3 + H_2O + \dot{O}H \qquad (8)$$

overall reaction

$$C_6H_5C_2H_5 + H_2O_2 = C_6H_5C_2H_3 + 2H_2O \qquad (13)$$

The proposed mechanism and the method of stationary states gave a kinetic equation[21] for the reaction rate which adequately describes the experimental data in the temperature range 500–620 °C:

$$-d[\mathrm{ETB}]/dt = k_{\mathrm{eff}}[\mathrm{ETB}][H_2O_2]$$

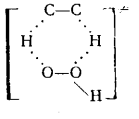
$$k_{\mathrm{eff}} = \frac{k_1 k_8}{k_{11}} = 0.35 \cdot 10^{16} \exp(-55300/RT) \text{ litre mole}^{-1}\text{s}^{-1}$$

The expression for k_{eff} does not contain the rate constant of reaction (5), so that the limiting step in chain propagation is reaction (8), which involves $HO_2^{\cdot}$.

The dehydrogenation of ethylbenzene by hydrogen peroxide (13) is a coupled reaction, since it is induced by the decomposition of H_2O_2 (the primary reaction). Both processes in the system are complex, and take place via a common intermediate active species, the $HO_2^{\cdot}$ radical,[7,22] and in the mechanism of the conjugated dehydrogenation a central position is occupied by the new elementary stage

$$\text{>CH–CH<} + HO_2^{\cdot} \rightarrow \text{>C=C<} + H_2O + \dot{O}H \qquad (5)$$

This reaction involves the formation of the six-membered transition state



which subsequently decomposes to give H_2O, alkene, and the free radical $^{\cdot}OH$, which is more active than the original $HO_2^{\cdot}$.

Thus the available theoretical and experimental data lead to a new and chemically specific mechanism of conjugated dehydrogenation, involving the primary (inducing) reaction of H_2O_2 decomposition and the secondary (induced) reaction of conjugated dehydrogenation.[6]

The use of H_2O_2 makes it possible to carry out effectively the incomplete dehydrogenation of cyclohexane to cyclohexene and cyclohexadiene; under other conditions this reaction is thermodynamically difficult.[23]

The conjugated dehydrogenation of cyclohexane by hydrogen peroxide can take place over a wide temperature range (450–630 °C) at different volume rates of supply of cyclohexane (0.1–1.0 h^{-1}) and H_2O_2 concentrations of 5–30% by weight. Under the optimum conditions at 580 °C, a conditional contact time $\tau = 4.2$ s, and a volume ratio of cyclohexane to aqueous H_2O_2 solution (20% by weight) of 1:3, the yields of cyclohexene and cyclohexadiene are 20% by weight and 4% by weight respectively, with a selectivity with respect to double bonds of 97% by weight.

Fig. 1 gives typical kinetic curves showing the consumption of cyclohexane and the accumulation of reaction products at 580 °C; the kinetic curves for the accumulation of cyclohexadiene and benzene are *S*-shaped.[23] These kinetic data indicate that the reaction products (cyclohexadiene and benzene) are formed by the successive dehydrogenation of the more saturated analogues. Thus the reaction products are formed in the successive stages:

		$\lg A_{\mathrm{eff}}$, cm^{3}mole^{-1}s^{-1}	E_{eff}, kcal mole^{-1}
$H_2O_2 +$	$C_6H_{12} \xrightarrow{k_{\mathrm{eff}\,1}} C_6H_{10} + H_2O$	24.95	63.0
	$C_6H_{10} \xrightarrow{k_{\mathrm{eff}\,2}} C_6H_8 + H_2O$	23.95	53.0
	$C_6H_8 \xrightarrow{k_{\mathrm{eff}\,3}} C_6H_6 + H_2O$	22.86	49.0

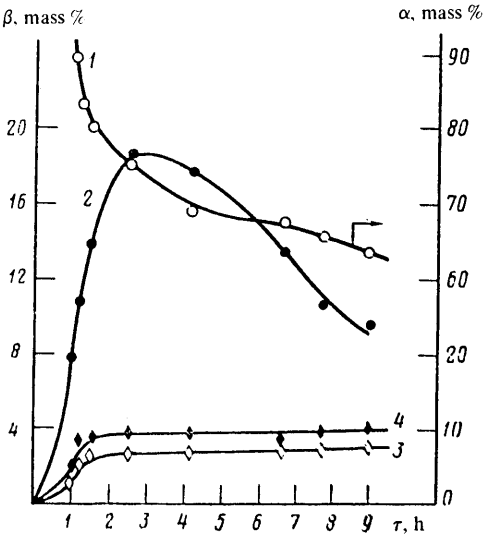


Figure 1. Kinetic curves giving the consumption (α) of cyclohexane (*1*) and the accumulation (β) of cyclohexene (*2*), cyclohexadiene (*3*), and benzene (*4*) in the coupled dehydrogenation of cyclohexane; $V_0 = 0.237$ h^{-1}, ratio C_6H_{12} : 20% aqueous H_2O_2 solution = 1:3 (by volume), 580 °C, τ is the conditional contact time.[23]

Each of the successive reactions described by the chain unbranched scheme (4), (8), and (11) represents a combination of the stages of chain initiation, propagation, and termination.

A system of kinetic equations providing an adequate description of the experimental data has the form:[24,25]

$$-\frac{d[C_6H_{12}]}{dt} = k_{eff\,1}[C_6H_{12}][H_2O_2]$$

$$-\frac{d[C_6H_{10}]}{dt} = k_{eff\,1}[C_6H_{12}][H_2O_2] - k_{eff\,2}[H_2O_2][C_6H_{10}]$$

$$\frac{d[C_6H_8]}{dt} = k_{eff\,2}[H_2O_2][C_6H_{10}] - k_{eff\,3}[H_2O_2][C_6H_8]$$

The overall dehydrogenation process is effectively described by a chain radical scheme with the following rate constants for the reaction of $HO_2^{\cdot}$ with cyclohexane and alkenes:

			lg A, $cm^3 mole^{-1} s^{-1}$	E, kcal $mole^{-1}$
$HO_2^{\cdot}$ +	C_6H_{12}			
	$C_6H_{10} \rightarrow \dot{O}H + H_2O$ +	C_6H_{10}	11.65	15.2
		C_6H_8	10.65	13.2
	C_6H_8	C_6H_6	9.86	9.2

The high selectivity of the process (95–99% by weight) and the absence of oxygen-containing reaction products makes it possible to eliminate a number of technological operations involving the separation of an appreciable quantity of components difficult to separate. Moreover, the high selectivity makes possible more complete utilisation of the raw materials.

An important task is the synthesis of pyridine bases and their derivatives, and the preparation of the corresponding N-oxides.[26] The realisation of the mechanism of chemical coupling in the oxidation of 4-ethylpyridine (4-ETP) by hydrogen peroxide[27] led to the development of a new method for obtained 4-vinylpyridine (4-VNP) and 4-vinylpyridine N-oxide. In a reaction vessel made entirely of quartz, in the range of volume rates of supply of 4-ETP 0.065–0.783 h^{-1} at a ratio of 4-ETP and 20% aqueous H_2O_2 solution of 1:3, the reaction takes place with a high selectivity up to 640 °C. Under the optimum conditions (620 °C), the yield of 4-VNP is 20.9% by weight with a selectivity of 92% by weight. Under the same conditions in a reaction vessel filled with quartz granules, the yield of 4-VNP increases considerably and amounts to 44.3% by weight with a selectivity of 96% by weight (Table 2).[28]

Table 2. Influence of the S/V ratio on the yield of 4-VNP.[28]

S/V ratio, cm^{-1}	Yield of 4-VNP (mass %) in relation to temperature, °C		
	600	620	640
Empty reactor, $S/V = 0.8$	15.2	20.9	21.8
With quartz packing, $S/V = 8.2$	39.1	44.3	46.7

The increase in the yield of 4-VNP when the reaction zone is filled with quartz granules is probably related to the fact that under the conditions studied, in a reaction vessel with quartz packing, the homogeneous decomposition of H_2O_2 is accompanied by the heterogeneous decomposition

$$H_2O_2 + \text{wall} \longrightarrow \dot{O}H + \text{wall–OH} \qquad (14)$$

With chain initiation by reaction (14) there is a gain of energy relative to the homogeneous reaction, equal to the heat of formation of the M–OH bond. Other conditions being equal, increase in the value of the factor S/V apparently leads to an increase in the concentration of active centres and hence in the yield of desired product.

The kinetic parameters of the overall reaction and the stage involving the reaction of 4-ETP with $HO_2^{\cdot}$ are given below:[29]

	lg A, $cm^3 mole^{-1} s^{-1}$	E, kcal $mole^{-1}$
4-ETP + H_2O_2 = 4-VNP + $2H_2O$	23.8	51.0
4-ETP + $HO_2^{\cdot}$ → 4-VNP + H_2O + $^{\cdot}OH$	10.8	10.2

In the liquid phase and at low temperatures, H_2O_2 can be used for the N-oxidation of pyridine bases, using organic acids and their anhydrides as catalysts. The synthesis of N-oxides without the use of a catalyst is of interest, since components giving decomposition products difficult to remove from the system are introduced.

The oxidation of 4-ETP by hydrogen peroxide showed that the maximum yield of 4-VNP N-oxide (Fig. 2)[30] is achieved at 300 °C. Under the optimum conditions at this temperature, the chief reaction product is 4-VNP N-oxide, the yield of which is 33% by weight with a selectivity of 98%. Increase in temperature from 200 °C to 300 °C increases the yield of N-oxide, probably because of an increase in the rate of the production of active centres in the decomposition of H_2O_2. Further increase in temperature from 300 °C to 400 °C leads to a decrease in the yield and the selectivity of formation of 4-VNP N-oxide. At a temperature of 400 °C, 19.8% 4-VNP, 91% pyridine, and only about 7% by weight of the N-oxide are formed.

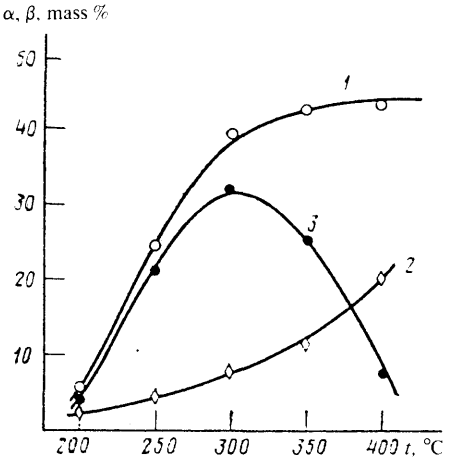


Figure 2. Influence of temperature on the degree of conversion (α) of 4-ETP (*1*) and the yields (β) of 4-VNP (*2*) and 4-VNP N-oxide (*3*) in the coupled oxidation of 4-ETP; $V_0 = 0.045\ h^{-1}$, [4-ETP]:[H_2O_2] = 1:3, H_2O_2 concentration 30% by weight.[30]

Thus depending on the oxidation conditions, the coupled oxidation of 4-ETP by hydrogen peroxide can be directed towards the formation of 4-VNP or its N-oxide.

The possible coupled dehydrogenation of alkenes by hydrogen peroxide was confirmed by the dehydrogenation of propene to allene and of isopentenes to isoprene.[31,32]

The familiar oxidative dehydrogenation of propene to allene in the presence of iodine[33] at a temperature of 625–700 °C is characterised by low yields of allene, 3.6% by weight, and a

low selectivity of its formation (6% by weight). In the case of the coupled dehydrogenation of propene under the optimum conditions (at 700 °C), the yields of allene and methylacetylene are ~20% by weight and 10% by weight respectively[34] (Fig.3). With increase in temperature above 700 °C, the yield of methylacetylene continues to increase, whereas that of allene decreases.

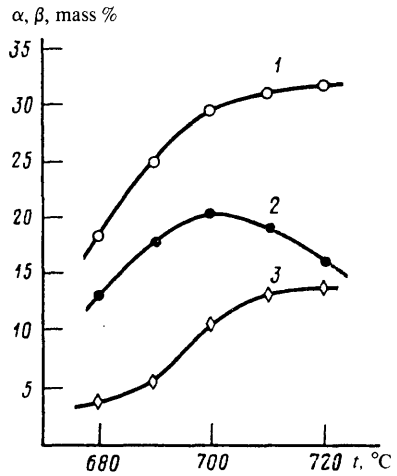


Figure 3. Influence of temperature on the degree of conversion (α) of propene (*1*) and the yields of allene (*2*) and methylacetylene (*3*) in the coupled dehydrogenation of propene; contact time 0.045 s.[34]

Fig.4 indicates that the coupled dehydrogenation of isopentenes with isomer compositions close to that of industrial fractions gives a fairly high yield of isoprene (25% by weight, with a selectivity of 75% by weight).[32] An advantage of this reaction over the oxidative catalytic dehydrogenation of isopentenes,[35] in spite of the relatively low selectivity, is the absence of the effect of retardation of the process by reaction products.

Of practical interest is the coupled dehydrogenation of industrial fractions of di-isopropylbenzene containing 57% *m*-di-isopropylbenzene and 34% *p*-di-isopropylbenzene by weight;[36] the yield of *p*-di-isopropenylbenzene in the dehydrogenation product reaches 30% by weight. The authors cited[36] compared the results with data on the catalytic dehydrogenation of di-isopropylbenzene on Shell-105 catalyst, and concluded that the yield and selectivity of the process are much higher in the coupled dehydrogenation of *p*-di-isopropylbenzene.

There are other examples of the preparation of alkenes of practical importance by coupled dehydrogenation, and these are considered below.

To some extent, the increase in the production of chloroalkenes[37] by existing technology is restricted by the loss of chlorine in byproducts, so that the development of methods for the dehydrogenation of chloroalkanes free from this disadvantage appears promising.

The oxidative dehydrogenation of ethyl chloride by air over a catalyst consisting of chromium oxide deposited on Al_2O_3 [38] is of interest in this connection. This process has a low yield and selectivity, however, since at the optimum temperature of 367 °C the yield of vinyl chloride is 17% by weight for a degree of conversion of 21% by weight. Some of these unsatisfactory features can be eliminated by the development of a new method for obtaining vinyl chloride, namely the coupled dehydrogenation of ethyl chloride by hydrogen peroxide.[39] Under the optimum conditions at a temperature of 450 °C, the yield of vinyl chloride is 37.8% by weight for a degree of conversion of 52% by weight, which is more than double the values for the process in Ref.38. It should be borne in mind the halogenoalkenes with more complex structures can also be synthesised in this way.

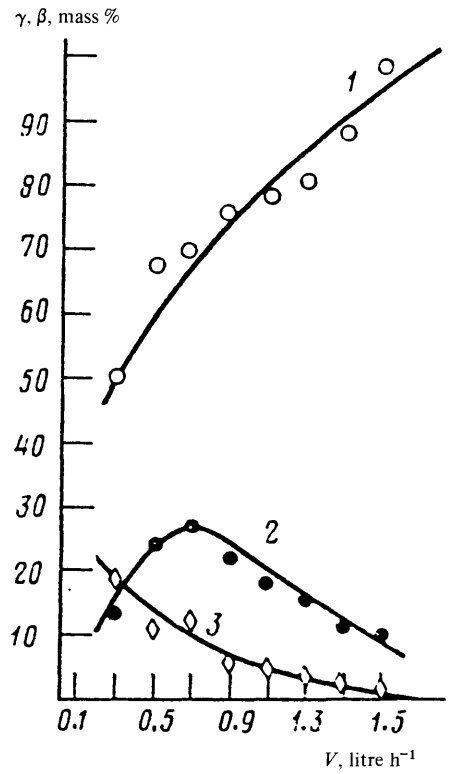


Figure 4. Influence of the rate of supply of the mixture of isopentenes and nitrogen ($V_{iso\text{-}C_5H_{10}} : V_{N_2} = 1:10$) on the selectivity of the coupled dehydrogenation (γ) (*1*), the yield of isoprene (*2*), and the total yield of side products (*3*); rate of supply of 20% aqueous H_2O_2 solution 0.185 ml h^{-1}, temperature 553 °C.[32]

The oxidative dehydrogenation of organic alcohols provides a relatively new approach to the development of industrial processes for obtaining aldehydes and ketones.[40–42] In this respect, the most successful from the technological viewpoint is the method for obtaining acetaldehyde by oxidising ethanol (at 350–490 °C) in an alcohol–air mixture in the presence of fused vanadium oxide or alkali metal vanadates catalysts with alkali metal sulphates or chlorides as promoters.[42] The yield of the desired product is 65.9% by weight, calculated on the alcohol passed, for a degree of conversion of 69.2% by weight. An unsatisfactory feature of the method[42] is the relatively low yield of the desired product and the increase in the complexity of the process with the use of an expensive catalyst.

To simplify the process and increase the yield of product, the oxidative dehydrogenation of C_2H_5OH has been carried out[43] by means of hydrogen peroxide by a conjugated mechanism. By varying different parameters of the reaction in the range 450–550 °C, it is possible, without using catalysts, to achieve fairly high yields of acetaldehyde (up to 87% by weight with a selectivity of not less than 97% by weight).

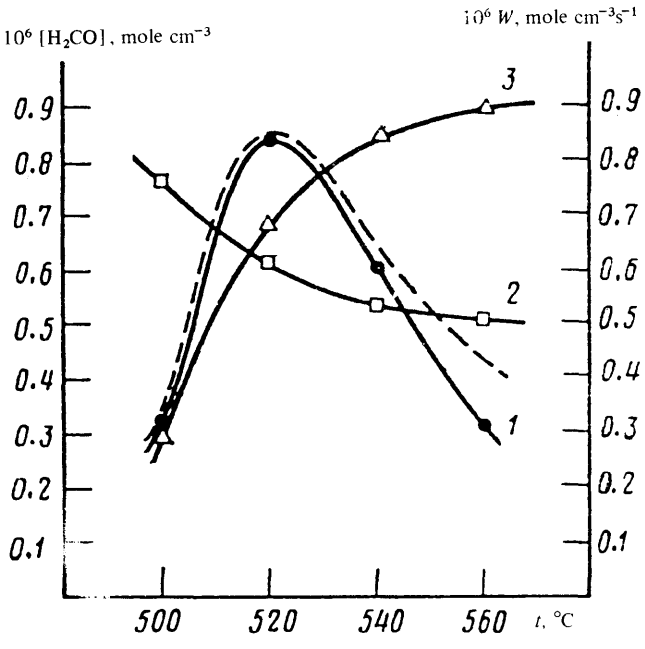


Figure 5. Temperature dependence of the H_2CO concentration (*1*) and the rates of accumultation (W) of $HO_2^{\cdot}$ (*2*) and $^{\cdot}CH_3$ (*3*) in the oxidation of methane by hydrogen peroxide; [CH_4] : [25% aqueous H_2O_2 solution] = 1 : 1, contact time τ = 1.2 s; the broken line gives the calculated curve for the accumulation of H_2CO.[50]

The high efficiency of the use of H_2O_2 in the oxidation of alcohols can also be illustrated by the dehydrogenation of s-butyl alcohol (2-BA) to methyl ethyl ketone (MEK). The oxidative dehydrogenation of 2-BA to MEK is now carried out using as catalysts metals such as gold and silver;[44,45] in the temperature range 520–600 °C, the yield of MEK is 70–85% by weight with a selectivity of 93–96% by weight. In spite of the high selectivity and degree of conversion to MEK, the presence of various side products such as acetaldehyde, acetone, diacetyl, CO, and CO_2 creates additional technological difficulties in the separation of MEK from the reaction medium.

In the liquid-phase oxidation of 2-BA,[46] although it is possible to avoid the use of precious metal catalysts, the characteristics of the process (the yield of MEK is 23.5% by weight with a selectivity of 79.4% by weight) are much inferior to those of the catalytic processes. Moreover, at 115–135 °C, it is necessary to use a pressure of 9–20 atm, to carry out the process and also to use initiating additives to decrease the induction period. The coupled dehydrogenation of 2-BA by hydrogen peroxide is free from most of these disadvantages, and makes it possible to increase the selectivity to 99% by weight, and to simplify the technology of the process, since it can be carried out at atmospheric pressure without using catalysts or special additives. The process is carried out in the gas phase at 460–560 °C with a yield of MEK of 26–44% by weight.

The possibility of obtaining unsaturated hydrocarbons and their derivatives by the conjugated decomposition of H_2O_2 and dehydrogenation of organic compounds indicates that this method is to some extent general.

2. The Coupled Oxidation of Methane to Formaldehyde by Hydrogen Peroxide

A large number of studies in the last ten years have been devoted to the incomplete oxidation of methane. The increased interest in the development of this method is due to the fact that methane is a practically inexhaustible natural raw material, whose possible utilisation will make it possible to satisfy completely the requirements of the national economy for methanol and formaldehyde.

The study of the mechanism of the oxidation of methane by oxygen in the presence of small quantities of H_2O_2 [47,48] has shown that H_2O_2 has a promoting action in the formation of formaldehyde. The intermediate species formed in the reaction are the free radicals $HO_2^{\cdot}$ and $CH_3O_2^{\cdot}$, whose transformations give the final reaction product H_2CO. In this reaction, H_2O_2 remains an intermediate product and accumulates in extremely small quantities.[47] The main oxidising agent is molecular oxygen, and the mechanism of the oxidation with added H_2O_2 does not differ significantly from the mechanism of the oxidation by O_2 in the absence of H_2O_2.

At the same time, the oxidation of various substrates by hydrogen peroxide in the gas phase takes place by a mechanism which is different from that involving molecular oxygen.[48]

The oxidation of methane to formaldehyde can be carried out with a high efficiency by the coupled oxidation of CH_4 in the presence of H_2O_2.[49,50]

The yield of H_2CO in the oxidation of CH_4 by hydrogen peroxide passes through a maximum with increase in the reaction temperature (Fig.5).[50] This form of the dependence is clearly related to the fact that H_2CO undergoes secondary reactions at temperatures above 520 °C. The maximum yield of H_2CO (39% by weight) calculated on the methane passed is reached at 520 °C, and at higher temperatures H_2CO is oxidised to CO. The concentration of CO in the reaction products increases with increase in temperature.

In the oxidation of methane by hydrogen peroxide, the following reaction becomes important:

$$CH_4 + OH^{\cdot} \rightarrow CH_3^{\cdot} + H_2O \quad \lg A = 12.5\ cm^3 mole^{-1} s^{-1}\ E = 2.0\ kcal\ mole^{-1} \qquad (15)$$

The concentration of $HO_2^{\cdot}$ in the H_2O_2–H_2O–CH_4 system will be determined by the ratio of the rates of reactions (5) and (15). At a molar ratio $CH_4 : H_2O_2$ = 1 : 1, corresponding to the optimum condition for obtaining formaldehyde, the ratio $[HO_2^{\cdot}]/[^{\cdot}OH] = 0.22 \times 10^4$, and the rates of the elementary reactions (5) and (15) with allowance for the reaction

$$CH_3^{\cdot} + HO_2^{\cdot} \rightarrow H_2CO + H_2O \qquad (16)$$

are practically equal and lie in the range $(0.46–0.60) \times 10^{-6}$ mole cm^{-3} s^{-1}.

Thus the radical $^{\cdot}OH$ formed in reaction (4) reacts with H_2O_2 and CH_4 at practically identical rates.

In this respect, the oxidation of CH_4 by hydrogen peroxide occupies a unique position, since in the presence of other compounds, for example ethylbenzene, cyclohexane, etc., the concentration ratio $[HO_2^{\cdot}]/[^{\cdot}OH] \gg 10^4$,[17] that is the main active centre is $HO_2^{\cdot}$. Under the optimum conditions for the

oxidation of methane, the concentrations of $^{\cdot}CH_3$ and $HO_2^{\cdot}$ are related by the inequality $[HO_2^{\cdot}]/[^{\cdot}CH_3] < 10^2$. This indicates that the cross recombination by reaction (16) is the main route to the formation of H_2CO. Other alternative routes to the formation of formaldehyde have been examined,[15] such as:

	$\lg A$, $cm^3 mole^{-1} s^{-1}$	E, kcal $mole^{-1}$	
$\dot{C}H_3 + H\dot{O}_2 \rightarrow CH_3\dot{O} + \dot{O}H$	13.51	≈ 0	(17)
$CH_3\dot{O} + \dot{C}H_3 \rightarrow H_2CO + CH_4$	13.4	≈ 0	(18)

The elementary stages (17) and (18) apparently do not play a signficant role, since the formation of the methoxy radical by reaction (17) should have led to the accumulation of methanol in the system by reaction (19), and this is not observed:[50]

$$CH_3\dot{O} + CH_4 \rightarrow CH_3OH + \dot{C}H_3 \qquad (19)$$

The addition of CH_3OH to the CH_4–H_2O_2–H_2O system leads to the unambiguous conclusion that CH_3OH is not an intermediate product of the selective oxidation of CH_4 by hydrogen peroxide.[50,51]

Under the conditions of the selective oxidation of CH_4 by hydrogen peroxide, the formation of CO and CO_2 is not observed, so that at relatively low temperatures and short contact times, the elementary stages involving their formation were not included in the proposed mechanism for the oxidation of CH_4.

In addition, the following stage was not taken into account in the oxidation scheme[15]

$$CH_4 + H\dot{O}_2 \rightarrow \dot{C}H_3 + H_2O_2 \quad \lg A = 13.3\ cm^3 mole^{-1} s^{-1}\ E = 18\ kcal\ mole^{-1}$$

since it has a low probability, because of its high activation energy. Chain termination as a result of the destruction of $^{\cdot}CH_3$:[51]

$$^{\cdot}CH_3 + wall \rightarrow CH_{3\,ads} \quad \lg A = 0.68\ s^{-1}\ E = 13.3\ kcal\ mole^{-1} \qquad (20)$$

was added to the elementary reactions (4), (5), (11), (12), (15), and (16).

The overall equation for the coupled oxidation of methane by hydrogen peroxide taking account of these stages has the following form:

$$CH_4 + 2H_2O_2 = H_2CO + 3H_2O \qquad (21)$$

These studies indicated that the most probable mechanism is one in which the chemical coupling between the decomposition of H_2O_2 and the oxidation of methane takes place through common intermediates, namely the free radicals $^{\cdot}OH$ and $HO_2^{\cdot}$.[50]

The proposed mechanism of formation of H_2CO was used to compile the following system of kinetic equations, which provide an adequate description of the experimental data (see Fig.5):[50]

$$-\frac{d[CH_4]}{dt} = k_{15}[CH_4][\dot{O}H]$$

$$\frac{d[\dot{O}H]}{dt} = 2k_4[H_2O_2][M] - k_5[H_2O_2][\dot{O}H] - k_{15}[CH_4][\dot{O}H] - k_{12}[\dot{O}H]$$

$$\frac{d[H\dot{O}_2]}{dt} = k_5[H_2O_2][\dot{O}H] - k_{16}[\dot{C}H_3][H\dot{O}_2] - k_{11}[H\dot{O}]_2$$

$$\frac{d[\dot{C}H_3]}{dt} = k_{15}[CH_4][\dot{O}H] - k_{16}[\dot{C}H_3][H\dot{O}_2] - k_{20}[\dot{C}H_3]$$

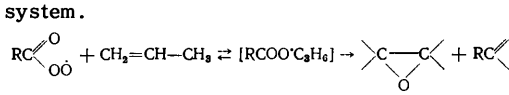
In the calculation, on the basis of Ref.52, it was assumed that the pre-exponential factor for the elementary stage (16) $\lg A_{16} = \lg A_{17}$. It was assumed that the activation energy of the recombination of the free radicals is close to zero.

Thus these studies gave the conditions for the selective coupled oxidation of methane by hydrogen peroxide to give formaldehyde, and a mechanism was proposed for the process.

3. The Coupled Oxidation of Propene by Hydrogen Peroxide

The catalytic epoxidation of alkenes by combined oxygen (ROOH, H_2O_2, peroxyacids) in the liquid phase has been discussed in a detailed review,[53] where it is possible to find detailed information on the kinetics and mechanism of the homogeneous catalysis of these processes in the presence of compounds of group V and VI elements.

Of particular interest is a single-stage method for obtaining alkene oxides by the conjugated oxidation of the alkenes with other organic compounds which are more easily oxidised, namely aldehydes, ketones, etc.[2,24] The active oxygen of peroxide radicals is used for the epoxidation of the alkene in this system.



These studies showed that it is possible in principle to carry out the epoxidation of alkenes by peroxide radicals, the simplest representative of which is the $HO_2^{\cdot}$ radical.

In recent years, from considerations of cost and availability, increasing use is being made of H_2O_2 as an oxidising agent for the selective oxidation of propene.[55] In the direct epoxidation in the liquid phase, however, hydrogen peroxide has a low reactivity, and it is therefore necessary to use various means of activating it, such as the reaction with carboxylic acids or with various inorganic anhydrides, which is accompanied by the formation of active compounds. In some studies,[56,57] the epoxidising agents used were peroxyacids formed by the reaction of H_2O_2 with formic and acetic acids. Of particular interest in this connection are the reactions involving the epoxidation of alkenes by peroxyacids at the moment of their formation from the acid anhydrides and H_2O_2. In the formation of alkene oxides by the reaction of the alkenes on the series of oxides of Ti, W, V, Ge, Mo, U, and Ru as catalysts, the most effective catalysts are tungsten oxides or tungstic acid, formed by the reaction of the oxides with H_2O_2.[58]

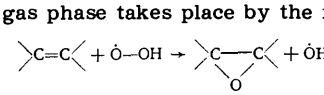
A non-trivial route to the synthesis of the important products propylene oxide, acrolein, and allene is provided by the gas-phase oxidation of propene by hydrogen peroxide by a coupled mechanism.[31,59]

Studies of the mechanism of the gas-phase and liquid-phase oxidation of hydrocarbons are giving a clear indication of the range in which a particular reaction path takes place, in relation to the specific conditions under which it is carried out.[60]

Thus depending on the conditions of the process (temperature, contact time, component ratio, H_2O_2 concentration, S/V ratio), the reaction of propene with hydrogen peroxide may lead to the epoxidation of propene, or to its oxidation to acrolein, or to coupled dehydrogenation.

In the range 500–580 °C, the main reaction is the coupled epoxidation of propene by hydrogen peroxide (Fig.6), and under the optimum conditions the average yield of propene oxide is 50 mass %.[59]

As already noted, in the gas-phase coupled oxidation by hydrogen peroxide in a flow system under stationary conditions, the $HO_2^{\cdot}$ concentration is greater than the $^{\cdot}OH$ concentration by several powers of ten. This fact, and also published data[53] on the epoxidation of alkenes by alkyl peroxide radicals, indicate that the epoxidation of alkenes by $HO_2^{\cdot}$ radicals in the gas phase takes place by the reaction:



The rate of epoxidation by alkyl peroxide radicals is determined by their structure. In the epoxidation of propene by hydrogen peroxide in the gas phase at 500–580 °C and a

contact time $\tau = 4.4$ s, the activity of $HO_2^{\cdot}$ as epoxidising species is greater than that of $RO_2^{\cdot}$.

The range 580–600 °C is an intermediate range in which the epoxidation of propene is accompanied by the simultaneous oxidation of propene to acrolein at a comparable rate. At 600–640 °C and $\tau = 1.2$ s, the main reaction product is acrolein, and its yield may reach 80 mass %.

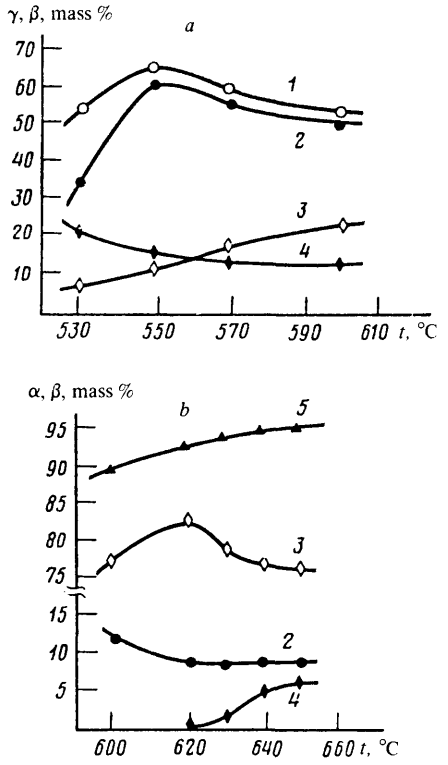


Figure 6. Temperature dependence of the selectivity (γ) (*1*), the yields (β) of propene oxide (*2*), acrolein (*3*), and side products (*4*), and the consumption of propene (α) (*5*) in its conjugated oxidation by hydrogen peroxide: *a*) 30 mass % H_2O_2, $V_{H_2O_2} = 1.3$ ml h^{-1}, $V_{C_3H_6} = 150$ cm^3 h^{-1}; *b*) 10 mass % H_2O_2, $V_{H_2O_2} = 3.78$ ml h^{-1}, $V_{C_3H_6} = 900$ cm^3 h^{-1}.[59]

Increase in temperature above 680 °C and $\tau = 0.045$ s leads to the formation of allene and methylacetylene as a result of the coupled dehydrogenation of propene (Fig. 3), and under the ultimate conditions the yields of these products are ~20% by weight and ~10% by weight respectively.[34]

Thus depending on the conditions, the coupled oxidation of propene may take place in three preferential directions:

$$CH_2{=}CH{-}CH_3 + H_2O_2 \rightarrow \left\{ \begin{array}{l} \rightarrow CH_2{-}\underset{\diagdown O \diagup}{CH}{-}CH_3 \\ \rightarrow CH_2{=}CH{-}CHO \\ \rightarrow CH_2{=}C{=}CH_2 \end{array} \right\} + \text{unwanted products}$$

In this system, as in the oxidations by hydrogen peroxide examined above, the coupling occurs according to schemes (1) and (2).[6]

It has thus been possible to determine the boundaries of the different mechanisms for the coupled oxidation of propene by hydrogen peroxide in relation to the conditions (temperature and contact time), and also to determine the intermediate ranges of the mechanisms of epoxidation and mild oxidation.

4. Coupled Oxidative Fixation by Hydrogen Peroxide

The problem of obtaining combined nitrogen from atmospheric nitrogen can now be solved by both reductive[61,62] and oxidative fixation. Several reactions for oxidising N_2 under severe conditions are known, for example the oxidation of N_2 by oxygen in an electric arc or plasma or under the influence of ionising radiation.[63] The direct oxidation of N_2 by oxygen is endothermic, and its realisation requires considerable expenditure of energy and gives low yields. It is therefore of considerable interest to develop nitrogen-fixation systems in which the principles of coupled reactions can be used.

The use of these principles in the oxidation of N_2 by hydrogen peroxide provides a new method for the fixation of nitrogen under conditions which are comparatively mild for reactions of this type.

The oxidation of nitrogen by hydrogen peroxide in a flow integral reaction vessel[64–66] makes it possible to obtain a yield of combined nitrogen of about 19% by weight.[68]

The mechanism of the oxidation of elementary nitrogen by hydrogen peroxide to N_2O includes a stage involving the reaction of N_2 with the $HO_2^{\cdot}$ radical, formed by the decomposition of H_2O_2:[69]

$$\begin{array}{l} H_2O_2 + \dot{O}H \rightarrow H\dot{O}_2 + H_2O \\ N_2 + H\dot{O}_2 \rightarrow N_2O + \dot{O}H \\ \hline N_2 + H_2O_2 = N_2O + H_2O \quad \Delta G^{\circ}_{298} = -4.5 \text{ kcal mole}^{-1} \end{array} \qquad (22)$$

Nitrous oxide was identified by mass spectrometry and gas-adsorption chromatography. The aqueous fraction of the reaction products, assumed to contain nitrogen-containing acids, was analysed by mass spectrometry and by a qualitative test with $AgNO_3$,[67] although the latter does not exclude the possible formation of unknown forms of combined nitrogen which react with $AgNO_3$ to give a precipitate.

The effective rate constant of reaction (22), determined from the experimental data,[70] is:

$$k_{22} = 10^{14.46} \exp(-45\,700/RT) \text{ litre mole}^{-1}\text{s}^{-1}$$

The second-order rate constant for H_2O_2, calculated from the overall equation

$$H_2O_2 + M \rightarrow \text{products}$$

is

$$k_{\text{eff}} = 10^{14} \exp(-46300/\text{RT}) \text{ litre mole}^{-1}\text{s}^{-1}$$

The proposed mechanism makes it possible to obtain relationships which provide an adequate description of the experimental data in the temperature range 450–600 °C at an H_2O_2 concentration in the aqueous solution of 15–30% by weight at supply rates of 1–5 litre h^{-1} nitrogen and 8–24 ml h^{-1} H_2O_2.[71]

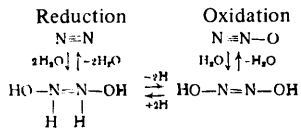
At 450 °C, the only product is nitrous oxide, the quantity of which amounts to 4% by weight, calculated on the original nitrogen. Beginning at 500 °C, the formation of combined nitrogen in the aqueous fraction of the reaction products is also observed, probably in the form of nitrogen-containing acids, the quantity of which increases to approximately 0.1% by weight with increase in the contact time.

Thus these studies have detected a new nitrogen-fixation system, which makes it possible to bind molecular nitrogen in an oxidative medium, as a result of chemical induction.

A distinguishing feature of the coupled oxidative fixation of N_2 by hydrogen peroxide is that the process takes place under relatively mild conditions compared with other similar reactions (at atmospheric pressure and at temperatures which are much lower than those usually required for the oxidation of nitrogen by oxygen).

In the biological fixation of molecular nitrogen, two different routes to its activation in the earliest stages of its fixation are possible: by reduction on the one hand and by oxidation on the other.[71] There is no proof, however, of oxidative fixation in the initial stages, although it is energetically more favourable.

According to Burris and Wilson, the following mechanism is involved in the initial stages of the biochemical fixation of N_2:[71]



In the oxidative part of this scheme, the question of the formation of nitrous oxide is not clear. Since hydrogen peroxide can induce chemical reactions, however, it has been possible to carry out the oxidative fixation of N_2 to N_2O by an energetically favourable path. All these studies make possible a new approach to the investigation of the mechanism of the biological fixation of N_2 and provide a new aspect to the nitrogen cycle.

III. CHEMICAL COUPLING IN LIQUID-PHASE OXIDATION BY HYDROGEN PEROXIDE

The catalytic decomposition of H_2O_2 in the liquid phase in the presence of iron(II) salts, discovered by Fenton,[72] is described by the following stepwise mechanism:[73]

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + \dot{O}H$$
$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + \dot{H}O_2 + H^+$$
$$Fe^{2+} + \dot{O}H \rightarrow Fe^{3+} + OH^-$$
$$Fe^{3+} + \dot{H}O_2^- \rightarrow Fe^{2+} + H^+ + O_2^{\cdot-}$$
$$Fe^{2+} + \dot{H}O_2 \rightarrow Fe^{3+} + HO_2^-$$
$$H_2O_2 + \dot{O}H \rightarrow H_2O + \dot{H}O_2$$
$$H_2O_2 + O_2^{\cdot-} \rightarrow O_2 + OH^- + \dot{O}H$$

Salts of copper, chromium, vanadium, cobalt, and other transition metals can also be used to catlayse the decomposition of H_2O_2.

The catalytic generation of $^{\cdot}OH$ radicals, taking place as a result of the alternate oxidation and reduction of iron(II) and iron(III) ions, makes it possible to obtain free radicals at temperatures much lower than in thermal homolysis.

The free radicals formed in the reaction can react with practically any organic compound in acidic solutions.[74]

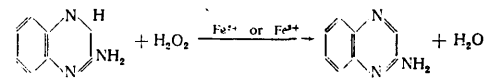
The oxidation of benzene in an aqueous solution of hydrogen peroxide in a Fenton system, which is taken as a classical example of a coupled process,[5] can be considered. The addition of an iron(II) salt to the C_6H_6–H_2O_2–H_2O system leads to the oxidation of benzene to phenol and biphenyl according to the following mechanism:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + \dot{O}H$$
$$Fe^{2+} + \dot{O}H \rightarrow Fe^{3+} + OH^-$$
$$C_6H_6 + \dot{O}H \rightarrow \dot{C}_6H_5 + H_2O$$
$$\dot{C}_6H_5 + \dot{O}H \rightarrow C_6H_5OH$$
$$\dot{C}_6H_5 + C_6H_5 \rightarrow C_6H_5 - C_6H_5$$

In this system, the phenomenon of induction is due to the fact that both reactions, that is the oxidation of C_6H_6 and Fe^{2+}, take place through common intermediate species, namely $^{\cdot}OH$ free radicals.[5]

As noted above, Fe^{2+} ions are effective catalysts for the decomposition of H_2O_2, so that the chemical conjugation in this system will not differ from that described in the previous section.[6]

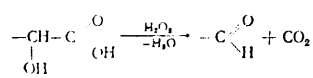
2-Amino-3,4-dihydroxyquinoxaline is comparatively readily dehydrogenated to give 2-aminoquinoxaline by H_2O_2 in the presence of traces of iron ions:[75]



The dehydrogenation takes place as a result of the reaction of the $^{\cdot}OH$ free radicals with the H(3) and H(4) hydrogen atoms of 2-amino-3,4-dihydroquinoxaline. The iron ions possibly bring about additional activation of the substrate molecule.

Free radicals also apparently play an important role in the degradation of carbohydrates by Ruff's method.[76]

The reaction of α-hydroxyacids with H_2O_2 in the presence of iron(III) salts takes place according to the overall equation:



In the successive transformation of D-glucose into D-arabinose

the stage involving the transformation of the aldonic acid into the 2-ketoaldonic acid is a dehydrogenation reaction. The role of H_2O_2 in this reaction is probably similar to that described above: the oxidising agents in this case are the highly active species formed by the decomposition of H_2O_2 in the presence of iron ions as catalyst.

The conjugated reactions of the decomposition of H_2O_2 and the oxidation of H_2CO and HCOOH in the presence of platinised graphites and Pt/(Pb with added Pb) was demonstrated in Ref.78. These studies showed that the ratio of the oxidation products is influenced significantly by the grade of graphite, the Pt deposition conditions, the reagent concentrations, and the percentage concentration of added Pb.

The detailed mechanism of the oxidation of dihydroxyfumaric and tartaric acids by hydrogen peroxide in the presence of iron and copper ions was studied in Ref.79.

In the gas phase under the conditions of conjugated oxidation by hydrogen peroxide, the $HO_2^{\cdot}$ concentration (2×10^{-9} mole cm^{-3}) is greater by many powers of ten than the $^{\cdot}OH$ concentration (7×10^{-13} mole cm^{-3}), and the ratio of the initial concentrations of $HO_2^{\cdot}$ and $^{\cdot}OH$ is about 10^4.[50]

In accordance with Eqn.(3), however, when the hydrogen peroxide is extensively diluted ($[H_2O_2] = 10^{-13}$ mole cm^{-3}), the system will contain chiefly $^{\cdot}OH$ radicals, and these will be responsible for the subsequent transformation of the substrate.

Since the reaction of the substrate with $^{\cdot}OH$ and $HO_2^{\cdot}$ radicals leads to the formation of different products, the composition of the products should depend on the degree of dilution of H_2O_2. According to Ref.80, $^{\cdot}OH$ brings about nonselective oxidation, whereas $HO_2^{\cdot}$ brings about the selective gas-phase oxidation of substrates by hydrogen peroxide. Thus in an RH–H_2O_2–H_2O system, decrease in the concentration of the reagents leads to an increase in the degree of conversion and a decrease in the selectivity of the reaction, whereas a decrease in the concentration of the reagents

usually leads to an increase in the selectivity and a decrease in the yield of the reaction products. This situation is observed not only in the case of extremely low concentrations of H_2O_2 in the aqueous solution, but also in a liquid-phase (Fenton) system, in which the principal active centre is $^{\cdot}OH$.

Thus in a Fenton system it is impossible in principle to achieve highly selective oxidation of the substrate.

IV. THE ABILITY OF HYDROGEN PEROXIDE TO INDUCE OXIDATION, AND POSSIBLE NEW APPLICATIONS

The mechanism of chemical coupling in oxidation by hydrogen peroxide can be formulated as follows: the ability of hydrogen peroxide to induce chemical reactions is due to its decomposition to give active centres which take part in another reaction which does not take place spontaneously (for example nitrogen fixation, dehydrogenation, etc.).

An interesting question is whether more complex peroxy-compounds such as organic hydroperoxides and peroxides can induce chemical reactions.

The mechanism of the chain decomposition of the initiator most widely used in chemistry, namely di-t-butyl peroxide,[81] can be examined in this connection:

$$(CH_3)_3COH + \dot{C}H_2C(CH_3)_2\dot{O} \rightarrow CH_2\!\!<\!\!\overset{O}{}\!\!>\!\!C(CH_3)_2$$

$$(CH_3)_3COOC(CH_3)_3 \rightarrow 2(CH_3)_3CO^{\cdot} \rightarrow 2(CH_3)_2CO + 2\dot{C}H_3 \rightarrow C_2H_6$$

$$\downarrow RH \qquad\qquad \downarrow RH$$

$$(CH_3)_3COH + \dot{R} \qquad CH_4 + R^{\cdot}$$

Di-t-butyl peroxide decomposes in the gas phase at 300 °C or in solution at pH ≥ 7 in different directions by a complex chain mechanism to give different reactions products: $(CH_3)_2COH$, $CH_2\!\!<\!\!\overset{O}{}\!\!>\!\!C(CH_3)_2$, CH_4, C_2H_6, and $(CH_3)_2CO$. The variety of chain decomposition paths is related to the formation of several active intermediate compounds, $(CH_3)_3CO^{\cdot}$, $^{\cdot}CH_2C(CH_3)_2O^{\cdot}$, $^{\cdot}CH_3$, and $R^{\cdot}$, whose transformation in the presence of the substrate (RH) gives a large number of side products.

Thus if attempts are made to use organic peroxides as components in conjugated reactions of mild oxidation, the above considerations related to the large number of active centres present a serious obstacle. In this system, the decomposition of the organic peroxide is accompanied by the chain oxidation of the substrate by different active centres to give the corresponding reaction products. Thus the absence of selectivity and the large number of chain reactions which can be initiated by organic peroxides create serious difficulties in the use of these hydroperoxides to induce reactions which do not take place spontaneously.

The ability of hydrogen peroxide to induce oxidative transformations of chemical substances as a result of chemical coupling not only extends the ways in which it can be used in new non-traditional directions but also leads to a deeper understanding of the mechanism of the action of H_2O_2 in many systems.

It can be confidently state that extension of the ranges of application of chemical coupling in general and in oxidation reactions in particular will stimulate progress in this field.

This will lead finally to the development of fundamentally new chemical-technological oxidation processes, corresponding to present-day requirements, that is the economic utilisation of energy resources and raw materials and an increase in the unit power of chemical reactors, without leading to environmental pollution. The low cost of H_2O_2 production by existing technology (chiefly by the anthraquinone method) provides a basis for increasing the use of H_2O_2 in modern industry. Thus the development of processes of oxidation by hydrogen peroxide corresponds to present-day requirements.

These studies raise another extremely important question for chemical technology, related to the unification of chemical production. It is surprising that unification, a powerful means of scientific and technical progress which has transformed many branches of industry, has hardly been introduced in chemical technology. This situation has probably arisen because almost every chemical reaction introduced has its own specific characteristics, which make it impossible to unify both chemical processes as a whole and individual technological units. To these characteristics can be added the use in industrial processes of specific catalysts with different compositions and structural properties, the formation of side products whose utilisation represents an independent problem, the purification of the desired product from side products, and the use of increased pressures and different phase states of the components of the reaction system.

The solution of the problem of the unification of chemical production will be found not in the development of separate chemical-technological processes differing considerably in their technological and chemical aspects, but in the development of chemical systems in which chemical reactions of the same type, having many common characteristics, can be realised.

Coupled reactions involving the oxidation of different substrates by hydrogen peroxide can justifiably be included among such chemical systems.

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Advances in the Development of Methods for the Epoxidation of Olefins

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Data obtained in recent years on the epoxidising agents and the mechanism of their interaction with olefins are surveyed. Different types of hydroperoxides as well as certain short-lived epoxidising intermediates of the molecular and radical types functioning *in situ* are examined.
The results of the stereospecific epoxidation of aliphatic and alicyclic compounds using the directing influence of functional groups (OH, COOH, R, SiR_3, etc.) are presented.
The bibliography includes 225 references.

CONTENTS

I.	Introduction	986
II.	Organic peracids	986
III.	Heteroanalogues of peracids	991
IV.	Inorganic peracids	991
V.	Epoxidation by hydroperoxides activated by electron-accepting substituents	992
VI.	Hydroperoxide epoxidation of olefins catalysed by transition metals	992
VII.	Stereoselectivity and regioselectivity of the hydroperoxide epoxidation	994
VIII.	Oxaziridines and heterocyclic epoxidising intermediates	997
IX.	The oxenoid mechanism. Carbonyl oxide and its analogues	998
X.	Some aspects of radical epoxidation	1000
XI.	The synthesis of oxirans based on intramolecular nucleophilic substitution	1001

I. INTRODUCTION

In terms of the character of the behaviour of the reagent and the substrate, the epoxidation of olefins has much in common with a whole series of reactions regarded as models of biological monoxygenation[1]—the oxidation of amines, phosphines, sulphides, Schiff bases, azo-compounds,[2-4] arenes,[5] alkanes,[6] etc. For this reason, new information about the synthesis and mechanism of action of any of the epoxidising agents acquires general theoretical importance for the development of ideas about liquid-phase oxidation as a method of organic chemistry and for the understanding of many biological processes.

The chemistry of oxiran has developed in two directions. One of these involves the industrial manufacture of the practically most important epoxy-compounds: the oxides of ethylene, propene, but-1-ene, butadiene, styrene, epichlorohydrin, and a wide assortment of aliphatic cyclic mono- and di-epoxy-compounds produced on a small scale.[2-7] The second direction is associated with the important role of oxirans in the living processes of the plant and animal world. Properties of epoxidised terpenoids, carotenoids, and steroids,[2] the juvenile hormonal activities of many natural and synthetic epoxy-compounds,[8-10] and the toxic and carcinolytic properties of epoxide-containing intermediates, formed in the oxidation of aromatic hydrocarbons,[11] have been widely investigated.

The physiological activity of many natural compounds containing epoxide oxygen has led to the problem of the development of the synthesis of their analogues and of a wide set of methods for stereospecific and regiospecific epoxidation. Considerable advances have been achieved in this field,[12] using on a wide scale the directing influence of neighbouring functional groups (OH, COOH, SiR, etc.). In its turn, the discovery of the stereochemical consequences of epoxidation has become a powerful means for the elucidation of the mechanism of the oxidation of various objects.

The aim of the present reivew was to give a systematic account of epoxidising agents and to elucidate the common features and differences in the mechanisms of their formation and action on olefins†.

The central place in the review is occupied by the expoxidation of olefins by peracids, which is the reaction most fully investigated in close association with solvation and association phenomena. The importance of data obtained in this connection is determined by the fact that many reactions involving hydroperoxides proceed, like the Prilezhaeva reaction, in a complex system of donor–acceptor interactions and combine both heterolytic and homolytic processes.

II. ORGANIC PERACIDS

Since the publication in 1974 of Prilezhaeva's fundamental monograph,[2] considerable progress has been achieved in the development of the methods of epoxidation by peracids. The methods for the synthesis of anhydrous peracids, in the first place the lower (C_1–C_4) peracids, based on the acylation of hydrogen peroxide by carboxylic acids or anhydrides in the presence of acid catalysts, have attracted constant interest.[13-16] Aqueous peracetic acid has acquired industrial importance.[17] Polymeric peracids have been synthesised by the interaction of carboxylated polystyrene with hydrogen peroxide in methanesulphonic acid.[18]

Crystalline perbenzoic acid is obtained by an improved method from benzoyl chloride[19] and by the alkaline hydrolysis of benzoyl peroxide.[20] Many olefins have been epoxidised by perbenzoic acid and its ring-substituted analogues at the instant of formation from the corresponding acid chloride and potassium peroxide in the presence of an interphase transfer catalyst.[21,22]

†A systematic consideration of the mechanism of the epoxidation of olefins by oxygen is outside the framework of this review.

m-Chloroperbenzoic acid is widely used for the synthesis of oxirans, which are sensitive to acids, in the presence of buffers (aqueous solutions of Na_2CO_3, $NaHCO_3$, Na_2HPO_4).[23-27]

There has been a continuation of studies on the synthesis of peracids by the oxidation with atmospheric oxygen of aldehydes: acetaldehyde, propionaldehyde, butyraldehyde, isobutyraldehyde,[28-30] *p*-toluic aldehyde,[31] pentafluorobenzaldehyde,[32] *p*-methoxycarbonylbenzaldehyde.[33]

Monopermaleic,[34-38] mono-, di-, and tri-chloroperacetic,[34-41] and 2,4-dinitroperbenzoic acids[42] have been used successfully for the epoxidation of electron-deficient olefins. The catalytic influence of organic nitrogen-containing bases (amines, pyridine, urea, guanidine, etc.) and inorganic bases on the reaction of acid anhydrides with peroxides has been demonstrated.[37,43-46] The method used in the employment of perphthalic acid has been improved.[47-49] Perphthalic acid *in situ* and in the crystalline form[47,50-52] as well as *p*-methoxycarbonylperbenzoic acid[33] are oxidants which are promising in practice. The epoxidising capacity of many peracids can be deduced from the relative rates of epoxidation of allyl bromide by peracetic, performic, monochloroperacetic, perbenzoic, monoperphthalic, and monopermaleic acids at 40 °C in acetic acid, which are respectively 1.0, 1.54, 1.70, 1.84, 8.7, and 15.1.[48]

The rate constants for the epoxidation of 1,4-dibromo-2-methylbut-2-ene with monochloroperacetic (at 10 °C) and dichloro-, trichloro-, and trifluoro-peracetic (at 2 °C) acids are in the ratios 1 : 13 : 1000 : 2700, although the differences between the overall efficiencies of these acids are not so significant. Furthermore, trichloroperacetic acid is more effective than its fluorine-containing analogue, since the enhancement of the electron-accepting influence of the substituents entails a decrease of the equilibrium concentration of peracid in the reaction of acid anhydrides with hydrogen peroxide, while the losses of active oxygen owing to decomposition increase.[45]

The most important application of peracids is epoxidation of electron-deficient olefins, which requires concentrated solutions of peracids, in many cases with added buffering bases. A series of studies have therefore been carried out on the mechanism of the interaction of peracids with olefins over a wide range of reactant concentrations and acid–base properties of the medium.[48,53-56] It was found that in multicomponent solutions with strong complex formation via hydrogen bonding the interaction of an olefin with a peracid proceeds as a complex process, the kinetics and direction of which depend to a high extent on the proton-donating and proton-accepting properties of the medium. Many of the experimental facts established under these conditions cannot be accounted for by the mechanism adopted, which presupposes the involvement in the reaction only of the unsolvated peracid molecule with an intramolecular hydrogen bond.[2]

It is striking that the epoxidation of the olefin proper competes as a rule with the spontaneous or olefin-induced decomposition of peracids. On the other hand, when the conditions are altered, the olefin can suppress the spontaneous decomposition of the peracid.[53-56] It has been shown by kinetic methods that the intermediate olefin–peracid complex disproportionates in many cases into isomerisation or epoxide ring-opening products, bypassing the oxiran formation stage.[57] The influence of solvation of the final result of the reaction has been demonstrated in relation to the epoxidation of diallyl maleate by permaleic acid in solvents of similar basicity: diethyl ether and tetrahydrofuran (THF).[58] Many oxirans are formed in the former case, while the epoxide ring opening products are formed in THF.

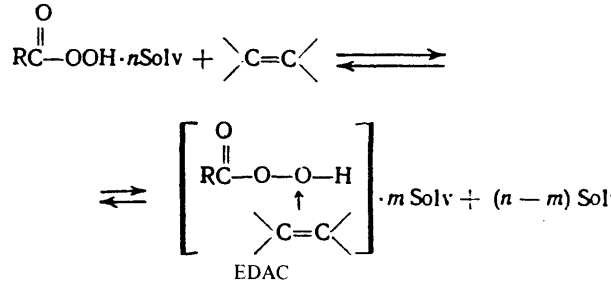
Experiments[54,66] on the epoxidation of olefins by peracids under the conditions of a gradual increase of the initial concentration of the base (dimethylformamide (DMF) in solution, which is known[59] to entail a change in the structure of the associated peracid species, are extremely instructive. Initially an increase of the DMF concentration reduces k_{epox}, as was to be expected,[2] and subsequently, in a rigorously defined range of its concentrations, the homolytic olefin-induced decomposition of acids is observed. Finally, the region of the induced decomposition is rapidly replaced by the region of the inhibition of the spontaneous decomposition of RCO_3H. The epoxidation constant k then increases significantly, although the degree of association of the peracid with the base increases.

The induction and inhibition of the decomposition of peracids by olefins depend specifically and to a large extent on the conditions governing solvation and association with the bases.[56] Purified peracids (95–99%) also decompose extremely vigorously under the influence of an olefin and, with increase of the concentration, the contribution of the decomposition process increases.

The epoxidation reaction and the accompanying reactions of peracids undergo autocatalysis or inhibition[55,56] up to the complete cessation of the reaction in the presence of still considerable concentrations of the reactants in solution.[60] The second order of the reaction is observed only at high acid concentrations, for example, when peracids synthesised from acid anhydrides are used. Under these conditions, the acid and oxiran (a base) formed in the reaction do not alter significantly the acid–base properties of the medium.

The so-called dilution effect is characteristic of the Prilezhaev reaction and the competing processes:[55,56,60,61] with decrease of the concentration of the reactants and following the dissociation of intermolecular hydrogen bonds, the specific rate (k) diminishes and the activation parameters (E_{act}, $\Delta S^{\neq}$) vary within wide limits. In many cases a kind of "organic" version of the salt effect is observed: an artificial increase of the concentration of associated species of the type of $RCO_2^-.BH$ increases the rate of the process,[56,60,62] which indicates an appreciable charge separation in the activated complexes.

It follows from the above that the olefin attacks the peracid incorporated in a system of intermolecular bonds. The donor–acceptor ("soft") interaction of the reactants competes with the "hard" complex formation reaction of the peracid via hydrogen bonding and, as a result of the substitution of the ligands, the solvent, or the base (Solv) in the solvation shell, the olefin produces a new association complex, a π-complex or an electron donor–acceptor complex (EDAC):



EDAC

The EDAC concentration is comparable to those of the reactant and, when present in a sufficient excess, the olefin is capable of fully solvating the peracid by accelerating the epoxidation process so that it is several times faster.[56,63-65]

The EDAC formation stage is responsible for the autocatalysis and inhibition of the epoxidation reaction. The autocatalysis is caused by the fact that the acid formed in the

reaction promotes the desolvation of the peracid, as a result of which the equilibrium in the formation of EDAC is constantly shifted to the right, controlling the rate of reaction as a whole. The autocatalysis may be manifested also as a consequence of the rapid increase of the molar ratio [olefin]/[RCO_3H] during the reaction.[56] The inhibition of the epoxidation can occur in its turn when the peracid is involved in complex formation with the oxiran as a base via hydrogen bonding (in the presence of highly pure, 95–99%, peracids) or with associated species with the type $RCO_2^-.\overset{+}{B}H$.[60] An increase of the excess of the olefin relative to RCO_3H and an increase of temperature weaken the inhibiting effect of the bases and their associated species.

Thus the rate and direction of the Prilezhaev reaction are determined by the nature of the peracid associated species. Many spectroscopic studies[61,66–69] and quantum-chemical calculations[2,69–72] have been devoted to the establishment of their structure. It is known that in inert solvents at low temperatures peracids form monomers with a weak intramolecular hydrogen bond, while in concentrated solutions they produced dimers.[2,66,67] The barrier to rotation about the O–O bond is insignificant (1.00–4.00 kcal mol^{-1}).[68–70] The available information about the geometry of the monomers is not unambiguous. According to the results of certain quantum-chemical calculations,[2,70] the peracid molecule is planar. However, it has been established that the *p* electron of the neighbouring nitrogen and oxygen atoms in the molecules of hydrazine, hydrogen peroxide, and many peroxy-compounds[68,73] tend to leave the energetically unfavourable eclipsed position (the *gauche*-effect).

The displacement of the *p* electrons of the external peroxide oxygen atom from the conjugation plane of the *p* and π electrons of the R–C(=O)–O– unit in the peracid molecule is reflected in the fact that, in terms of its proton activity, it is greatly inferior (by 3.5 orders of magnitude) to the related normal acid.[2,68] These ideas agree with the calculation of dipole moments of RCO_3H by Swern and co-workers[74] (the dihedral angle θ between the COO and OOH planes is 72°) and also with quantum-chemical calculations[70,71] (θ = 40–60°). It has been noted that the *s-trans*-conformation is just as characteristic of peractic acid as the *s-cis*-conformation.[72] The *s-trans*-structure has been attributed to *o*-nitroperbenzoic and perpelargoric acids (θ = 146°) on the basis of X-ray diffraction analysis.[70]

Calculation has shown[69] that the $RCO_3H.RCO_2H$ associated species is much more stable than the dimer $RCO_3H.RCO_3H$ and that not only the carbonyl[71] but also the peroxide oxygen atom, linked to the >C=O group, can function as the proton acceptor in the formation of the latter dimer.

Experimental and calculated data make it possible to infer that the peracid molecule can exist in both *syn*-chelated and transoid forms. It must be assumed that in solutions the conformation of RCO_3H is influenced significantly by the nucleophilic effects of the solvent, the reagent, and other components on the acid proton and the peroxide oxygen atom.

The infrared spectra of dilute solutions of peracids show that in basic solvents (dioxan, THF, etc.) the free RCO_3H monomer is virtually absent—the ν(OH) band undergoes a 70–90 cm^{-1} bathochromic shift.[67–69] The ^1H NMR spectra of solutions of *m*-chloroperbenzoic (85%) and perlauric (99.5%) acids in the concentration range 0.2–2 M also lead to the conclusion that in a basic medium the peracid is wholly solvated, although the degree of proton transfer to the solvent varies within a wide range.[61,69] At a sufficiently high concentration, ensuring the emergence of the peracid molecule from the solvent cage, the signal of the protons becomes narrow and intense, which indicates their equivalence, attained as a consequence of the rapid exchange in the chain of hydrogen bonds. Acid admixtures appreciably accelerate the formation of associated chain species.

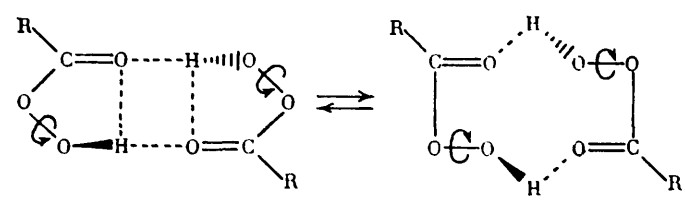
Spectroscopic data and the general theoretical ideas about the acid–base interactions in organic media[60] permit the conclusion that the state of the solutions of peracids, containing admixtures of acids and bases, is characterised by a multiplicity of different types of associated species, differing in the degree of proton transfer to the base (B) or the conjugate base (A), although, within certain concentration ranges and for certain ratios of the acid and basic components, specific dominant forms of the associated species are produced.

Using the "from the structure of the peracid to the mechanism" principle[2] as a guide, the probable mechanisms of the interactions of olefins with peracids can be represented as follows.

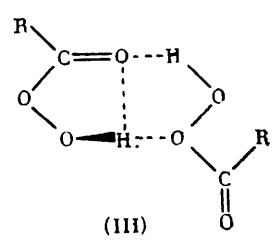
In inert solvents, at low concentrations of the peracid, which exists mainly in the monomeric form, the Bartlett–Lynch mechanism probably operates.[2] However, the character of the proton transfer remains obscure. Thus dilution of the solution with pure (99%) peracid, which leads to the dissociation of the intermolecular hydrogen bonds, reduces the k_{eff} for the epoxidation reaction, although it was to be expected that an increase of the fraction of the monomer would have the opposite influence. The rate constants for the epoxidation of hex-1-ene in benzene (1 M, 30 °C) at perlauric acid concentrations of 1.5 and 0.5 M are 1.15×10^{-4} and 0.84×10^{-4} litre mol^{-1} s^{-1} respectively. Thus, even a weak intermolecular interaction between the peracid monomers and dimers exerts an appreciable electrophilic cooperative effect on the elimination of the acid anion.

The preferred migration of the proton in the "olefin–peracid" transition state to the "internal" peroxide and not the carbonyl oxygen atom has been demonstrated by calculation.[75]

Peracid dimers appear in solution with increase of concentration. The combination of cisoid and transoid conformers leads to the following possible structures:

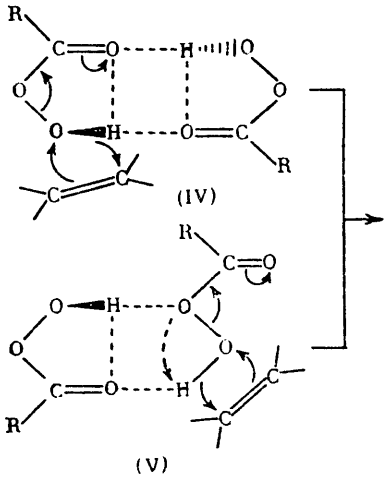


(I) (II)



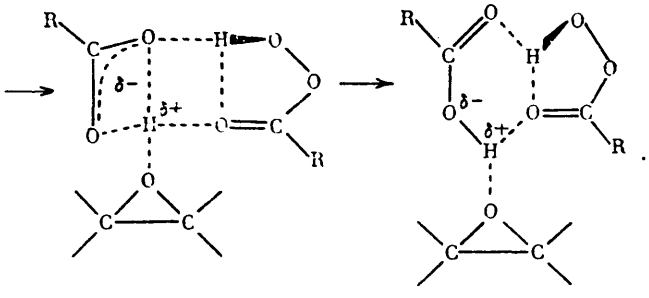
(III)

The formation of dimers promotes the epoxidation reaction—k_{eff} increases:



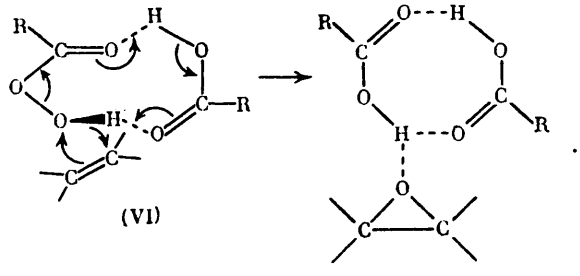
(IV)

(V)



The dimeric form II is less favourable in the epoxidation reaction, since the approach of the olefin to the external peroxide oxygen is blocked by the second peracid molecule.

In the presence of acids, associated species of the type $RCO_3H.RCO_2H$ are formed together with the dimers RCO_2H. $.RCO_2H$, which appreciably accelerates the epoxidation reaction:

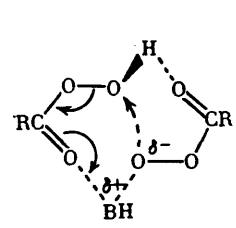


(VI)

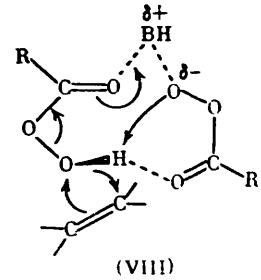
It can be seen, that in conformity with the minimum displacement principle,[76] only intermolecular proton transfer leads to the optimum structure of the acid dimer.

Small amounts of added base are inserted in the acid associated species without causing their complete decomposition#.[59] The base binds to the proton in the dimer (I) and promotes the transformation of the *s-cis*-conformers into the *s-trans*-conformers (VII) and permits the donor–acceptor interaction of the peroxide atoms and in the limiting case the decomposition of the peracid.[61]

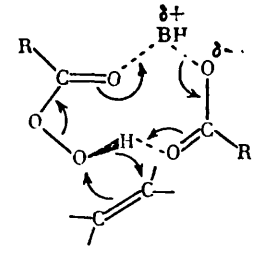
#The associated species $RCO_2^-Na^+.RCOOH$ is known to be very stable.[77]



(VII)



(VIII)

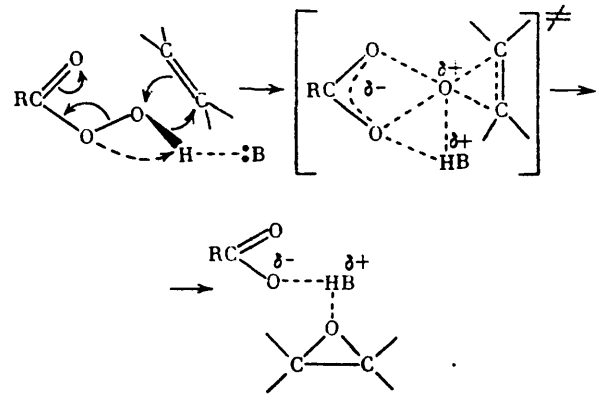


(IX)

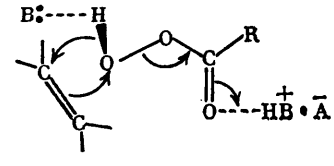
On the other hand, in the presence of an olefin, the epoxidation reaction behaves as the competing pathway (VIII). The epoxidation mechanism (IX) develops similarly when the base is incorporated in the associated species $RCO_3H.RCO_2H$.

The intramolecular migration of the proton in (VIII) and (IX) is less favourable than the intermolecular migration. In the intramolecular transfer in (VIII) the base would have been found to the weaker acid (RCO_3H) while in (IX) an anomalous acid dimer would have been formed.

At high concentrations of the base or after dilution with a basic solvent, the chelate complexes of the peracid decompose.[59] The peracid molecule linked to the base apparently exists, like peresters and acyl peroxides,[68,72] in the form of *s-trans*-conformers and proton transfer takes place in a solvent cage with participation of the conjugate base of the acid:



In the presence of large amounts of acids and bases, the relay proton transfer is most probable:



In the chelate complexes (VI), (VIII), and (IX) the non-coplanar attack on the olefin can induce the radical decomposition of the peracid with formation of carbon dioxide and an alcohol.

The data obtained in quantum-chemical and stereochemical studies of the π-complex and the "olefin–peracid" transition state[75] are fully consistent with the ideas described above, which were developed at a qualitative level. However, it has been stipulated that the attack by the peracid is directed to the carbon of the olefin double bond and not to the π-electron cloud.[78,79]

The study of the kinetics of the epoxidation of deuteriated styrene derivatives[79] established that the replacement of H by D in the α-position hardly influences the rate of reaction ($k_H/k_D = 0.99$), while deuteriation of the β-carbon atom leads to an appreciable isotope effect ($k_H/k_D = 0.82$). Since the secondary isotope effect is caused in the given instance by a change in the hybridisation of the carbon atom in the olefin double bond ($sp^2 \rightarrow sp^3$), the authors assume that only the formation of the C_β–O bond is manifested in the transition state. However, according to the proposed mechanism, the peracid functions as a nucleophile, which is consistent with the fairly well established fact that the peracid is electrophilic and the olefin nucleophilic.[2] One cannot rule out the possibility that the absence of an isotope effect in the deuteriation of the C_α atom is caused by the shielding influence of the bulky phenyl group.

For the interpretation of the structure of the "olefin–peracid" transition state (TS), it is useful to employ the idea that the elements of π- and σ-complex formation are combined in the structure of the protonated epoxide ring.[80,81] The reaction constant for the epoxidation of a number of olefins by a strong peracid, for example, monopermaleic acid,[56] is small in absolute magnitude ($\rho^* = -0.56$). According to the Bell–Evans–Polanyi principle, the nature of the transition state is in this case closer to that of the starting materials and the π-component predominates in its structure. The epoxidation by a weak peracid (peracetic acid)[56] is characterised by a high constant $\rho^* = -1.39$, the transition state resembles the final products, and the contribution of σ-complex formation increases. In terms of the molecular orbital (MO) method, the ring formation process is represented as a combination of the donor–acceptor overlapping of the bonding π_b orbital of the olefin with the σ^*_{O-O} orbital of the peracid and the dative interaction of the non-bonding orbital of the peroxide oxygen with the antibonding π^*_{antib} orbital of the olefin. The fact that the substituted propenes $CH_2{=}CH{-}CH_2{-}X$ (X = halogen or OR) are epoxidised with greater difficulty than the related 1,4-disubstituted but-2-enes, contrary to the hypothesis that the influence of the substituents is additive, can be accounted for from this standpoint.[82] The synchronous occurrence of the two types of orbital overlapping on formation of the oxiran ring apparently imposes definite requirements on the symmetry of the activated complex, as a result of which the asymmetrically substituted olefins are in a less favourable position.

In the alkaline epoxidation of polar multiple bonds, the sign of ρ^* changes[83] and the dative interaction becomes of decisive importance in the cyclisation stage.

Certain new stereochemical features of the reactions of olefins with peracids have been established, indicating that the rate of reaction and its direction are determined not only by electronic factors but also by the relaxation properties of the reactant molecules incorporated in the associated structure of the solution.

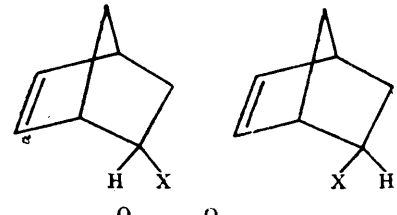
Previously it was believed[2,84] that the rate of reaction of the aliphatic compounds is independent of the steric influence of the substituents (especially alkyl substituents) at the reaction centre. However, it was found[85] that an alternative effect is characteristic of aliphatic reactants, namely the dependence of k_{eff} on the number of carbon atoms in the olefin (C_6–C_9) and the peracid (C_1–C_{12}) is represented by broken lines. Consequently, the alternating changes in the conformation of the R residue and of the molecule as a whole as the carbon chain grows can exert an unfavourable influence on the stage in which the reactants approach one another and are coordinated.

It is of interest to note that in a basic solvent (ethyl acetate) the long-chain RCO_3H proved to be unexpectedly more effective oxidants than the lower peracids (R = H or CH_3). This finding can be explained by the hydrophobic character of the massive alkyl component, which hinders the solvation of the peracid molecule. On the other hand, in an inert solvent (benzene), which does not solvate peracids, the strength of the latter is determined by the electronic factor: with increase of the bulk of R, the epoxidising capacity of RCO_3H diminishes.

Steric hindrance due to the increase in the size of the reactant molecules is observed also in other reaction series. Thus the loss of active oxygen in the epoxidation of allyl bromide by peracids in the series peracetic–perpropionic–perbutyric–perlauric increases owing to their induced decomposition[48] and the rate of epoxidation of the first olefin double bond in the diallyl esters of dicarboxylic acids $ROOC(CH_2)_nCOOR$ [58] increases only with increase of n from zero to two; subsequently k_{epox} diminishes.

The solvation of functional groups remote from the reaction centre has a significant influence on the rate of epoxidation.[58,82,86] Such solvation probably causes, by the increase of size, some loss of degrees of freedom by the reactant molecules and diminishes the probability of their effective collisions. In particular, it has been established that the rate of epoxidation (k_2) of the monoepoxides of the diallyl esters of dicarbocylic acids is much lower than the rate of formation (k_1) of the first epoxide ring ($k_1/k_2 = 4$).[58] When $n \geq 2$, this fact cannot be accounted for by the electron-accepting influence of the epoxide ring.

The decrease of the rate of epoxidation of the remote olefin double bond in sorbic acid esters[82] is caused by the increase in the size of the alcohol residue in the ester group. The character of the influence of the functional groups on the rate of epoxidation of the *exo*- and *endo*-isomers of substituted norbornanes is also determined by the solvation conditions:[86]



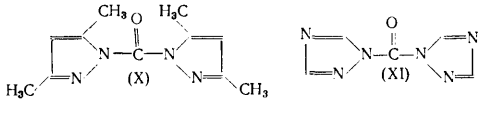
In the *exo*-position the substituents which tend to become involved in complex formation via hydrogen bonding (CO_2H, $CONH_2$) are "available" for the formation of intermolecular hydrogen bonds, while in the *endo*-position they are shielded by the carbon skeleton of the molecule. For this reason, the catalytic effect of the COOH group and the inhibiting influence of the basic $CONH_2$ group are manifested much more strongly in the *exo*-position. Certain nucleophilic groups ($CONH_2$, OH) in a series of *endo*-derivatives of norbornene exhibit an anchimeric cooperative effect on the epoxidation reaction.

III. HETEROANALOGUES OF PERACIDS

Derivatives of carbonic acid $X-\overset{\overset{O}{\|}}{C}-OOH$, where X represents nitrogen- or oxygen-containing functional groups, and the compounds $X-\overset{\overset{NR(H)}{\|}}{C}-OOH$ containing the azomethine group instead of the carbonyl group are close to organic peracids as regards their effectiveness. A characteristic feature of their chemical behaviour is an increased tendency towards decomposition[87,88] caused in the first place by the catalytic influence of the basic nitrogen-containing functional groups and rings[56,61] and in the second place the tendency towards decarboxylation of the monofunctional derivatives of carbonic acid, formed in the stage involving the transfer of active oxygen to the substrate. The decomposition of the heteroanalogues of peracids[87] leads to the formation of singlet oxygen, which is significant evidence for the heterolytic reaction mechanism and is consistent with the ideas developed by the present author.[56,61] The ability of the olefin to inhibit the decomposition reaction has also been noted.

Compounds of the above series are synthesised from hydrogen peroxide and the reaction concerned involves either nucleophilic substitution at the carbon atom of the carbonyl group or the nucleophilic addition to the azomethine or nitrile group.

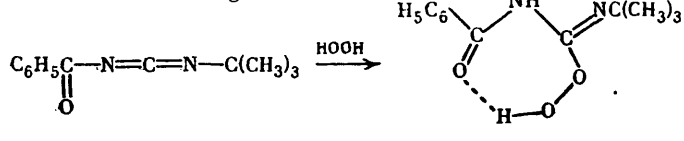
It has been noted that, in contrast to SeO_2, dialkyl carbonates and CO_2 do not form peracids in their reactions with H_2O_2, whereas peroxycarbamic acids, capable of epoxidising reactive alkenes of the type of cyclohexene, are formed from derivatives of dimethylpyrazole (X) and 1,2,4-triazole (XI):[87,88]



Among the hydroperoxy-derivatives of carbonic acid, mention should be made of *N*-benzoylperoxycarbamic acid ($C_6H_5-\overset{\overset{O}{\|}}{C}-NH\overset{\overset{O}{\|}}{C}-OOH$) and *O*-benzylperoxycarbonic,[89] and *O*-ethylperoxycarbonic acids[90,91] ($ROC(=O)OOH$), obtained by treating hydrogen peroxide with benzoyl isocyanate ($C_6H_5\overset{\overset{O}{\|}}{C}-N=C=O$) in the first case and by compounds of the type $R-O-\overset{\overset{X}{|}}{\underset{\underset{O}{\|}}{C}}-X$, where R = $C_6H_5CH_2$ or C_2H_5 and X = Cl or $OCOCH_2C_6H_5$, in the last two cases.

The rates of epoxidation of *trans*-stilbene at 25 °C in benzene by *O*-benzylperoxycarbonic, perbenzoic, and *m*-chloroperbenzoic acids are in the ratios 7.12 : 4.27 : 15.0, while *N*-benzoylperoxycarbamic acid is 200 times more effective than perbenzoic acid, which is undoubtedly assisted by the possibility of the elimination of carbon dioxide from the "olefin–peracid" complex.

Carbodiimide is less reactive in the reaction with hydrogen peroxide than isocyanates and gives rise to peracid heteroanalogues only in the presence of electron-accepting substituents at the nitrogen atom:[87]



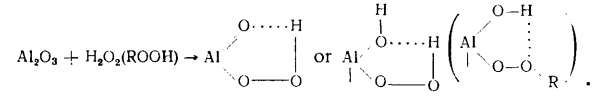
A similar peroxy-group is produced by cyanates ($RO-C\equiv N$),[87] benzonitrile,[92] and cyanamide ($H_2N-C\equiv N$),[93] which react with hydrogen peroxide via Paine's mechanism.[2] A method for the epoxidation of styrene by a mixture of acetonitrile and hydrogen peroxide in an alkaline medium with added Na_2HPO_4 has been proposed.[94]

A most powerful oxidant with the tentative structure $[(CH_3)_2\overset{+}{N}=CH-OOH]P\bar{O}_2Cl_2$, which epoxidises cyclenes at −80 °C, is formed in the H_2O_2–Vilsmeier reagent system.[95]

IV. INORGANIC PERACIDS

Inorganic peracids are employed as a rule at the instant of formation on treatment of the anhydrides (oxides), chlorides, and salts of acids with hydrogen or alkali metal peroxides. The possibility of their application is limited by the high acidity of the medium, which promotes the opening of the epoxide ring, and by the tendency towards decomposition, which increases in parallel with increasing strength of the peracids. A decrease of the pH of the medium is attained when acid salts are used. Naturally, the oxidising power of the hydroperoxide intermediate is then also lowered.

Vanadium, molybdenum, tungsten, selenium,[96–105] boron,[106] arsenic,[107] and aluminium[108] oxides have been used for epoxidation. They give rise to an epoxidising agent, for example:



The fact that the peracid and not hydrogen peroxide is involved in the epoxidation reaction has been confirmed by the kinetics of the oxidation of allyl bromide,[97] allyl alcohol,[98] and maleic and fumaric acids and their salts[99–103] by hydroperoxide derivatives of orthovanadic, tungstic, and molybdic acids. The above unsaturated acids are not oxidised by organic peracids.

Many derivatives of stilbene, chalcone, and acenaphthylene have been epoxidised by alkane- and arene-persulphonic acids,[21] obtained by the interaction of the corresponding chlorides ($C_6H_5SO_2Cl$, Cl_3CSO_2Cl, $CH_3C_6H_4SO_2Cl$, etc.) with potassium peroxide in the presence of a crown-ether as the phase-transfer catalyst. The broad spectrum of the activity of these reagents is probably due to the fact that they can function both in the undissociated state (RSO_2-OOH), executing an electrophilic attack on the multiple bond of, for example, stilbene, and in the form of the corresponding peroxide-anion (RSO_2-OO^-), which is capable of attacking the polar olefin double bond of the chalcone, like the hydroperoxide anion (HOO^-).

Peroxymonophosphoric acid epoxidises *trans*-stilbene but does not permit the isolation of cyclohexene, styrene, and α-methylstyrene oxides[109] because of the high acidity of the medium. It has been noted that the rates of epoxidation of *trans*-stilbene by H_3PO_5 and CH_3CO_3H are comparable, while the Baeyer–Villiger reaction is 100 times faster when perphosphoric acid is used. These differences are due to the fact that the rate-limiting stage in the oxidation of a ketone, namely the rearrangement of an acylhydroxyalkyl peroxide, is sensitive to acid catalysis, which is undoubtedly more effective in perphosphoric acid.

Benzeneperoxyseleninic acid has found application in the synthesis of epoxides.[96,110,111] Mixtures of areneseleninic acid ($X=C_6H_4Se(=O)OH$, where X = NO_2, Cl, COOH, etc.) and

30–90% hydrogen peroxide epoxidise alkenes in the presence of phosphate buffer. The acid is used in catalytic amounts (0.5–5%).

It has been shown in relation to allyl alcohols and diolefins that a perseleninic acid is less stereoselective and regioselective than carboxylic peracids and alkyl hydroperoxides, which indicates its highly electrophilic nature.

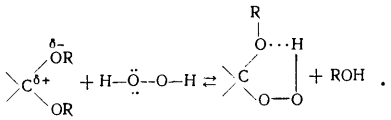
Presumably the replacement of the OH group by OOH in the acid reagent takes place also in the epoxidation of tetracyanoethylene with hydrogen peroxide containing added $HClO_4$.[112]

Triphenylsilyl hydroperoxide (Ph_3SiOOH) behaves like peracids in relation to olefins, ketones, and allyl alcohols,[109] although its structure is similar to that of alkyl hydroperoxides. The comparatively high epoxidising capacity of Ph_3SiO_2H is due to the dative interaction of the lone electron pairs of the neighbouring atoms (O, N, and halogen) and the unoccupied *d* orbitals of silicon, which is typical for silicon compounds.

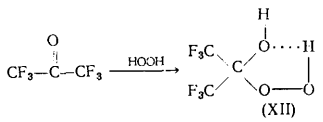
V. EPOXIDATION BY HYDROPEROXIDES ACTIVATED BY ELECTRON-ACCEPTING SUBSTITUENTS

The replacement of carbonyl oxygen in the peracid molecule by another, stronger electron acceptor (OH, OP, NP_2) leads to a series of hydroperoxides, which have lower oxidation potentials than peracids but do not lose their epoxidising capacity.

Rebek proposed a series of hydroperoxyethers,[87,113] obtained by the interaction of acetals, ketals, or orthoesters with 90% hydrogen peroxide, as epoxidising agents:



The products of the addition of hydrogen peroxide to the carbonyl group in ketones containing electron-accepting groups, namely tetrachloro-,[114] hexachloro- and hexafluoroacetones,[87,115,116] are more effective oxidants:



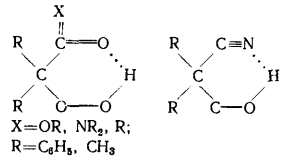
(XII)

The reagent (XII) epoxidises cyclic and acyclic olefins at 0 °C with a 60–93% yield of oxirans, while at an elevated temperature it oxidises ketones and esters.

A series of oxo-compounds (chloral, benzoin, acetophenone, acetoacetic ester, pentachlorobutanone, glucose, etc.) have been investigated in the epoxidation of cyclododecatriene and dicyclopentadiene.[117,118] It was found that the best results are achieved at 50–60 °C in the absence of a solvent. The rate of reaction is to a large extent determined by the diffusion constant. In particular, chloral generates the most reactive hydroperoxide, superior in its strength to the adduct of hexachloroacetone. Reagents of the above type make it possible to obtain monoepoxides in 25–95% yield virtually without an admixture of diepoxides.

The azomethine group in pyridinium salts and Schiff bases behaves similarly to the carbonyl group of ketones in the presence of hydrogen peroxide,[87] but the yield of oxirans is then low (3–45%).

The α-hydroperoxides of ketones, esters, nitriles, and amides,[119] formed in their autoxidation in the presence of potassium t-butoxide,[120] are epoxidising agents whose strength is comparable to that of peracetic acid:



X=OR, NR_2, R;
R=C_6H_5, CH_3

These reagents act stereospecifically on olefins—the *syn*-epoxyalcohol is formed preferentially in the epoxidation of 2-cyclohexanol. However, in contrast to peracids, the ester α-hydroperoxide oxidises *trans*-stilbene more easily than the *cis*-isomer, while *trans*-β-methylstyrene is oxidised more readily than cyclohexene. The selectivity of the reagent diminishes greatly when chloroform is replaced by benzene as the solvent.

The weak epoxidising capacity of the hydroperoxy-derivative of pyrazole, which is structurally similar to natural products, namely 4a-hydroperoxides of flavin, has been demonstrated.[121]

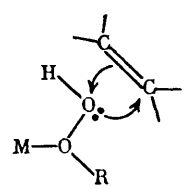
It is of interest to note the results of the oxidation of styrene by atmospheric oxygen on the styrene–oxygen copolymer as the template.[122,123] The dioxetan fragment of the copolymer

has been considered as the possible epoxidising group. An alternative version of the mechanism may involve epoxidation by the hydroperoxy-groups produced from the CH and CH_2 units in the α-position relative to the benzene ring or the peroxide bridge.

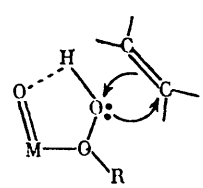
VI. HYDROPEROXIDE EPOXIDATION OF OLEFINS CATALYSED BY TRANSITION METALS

The state and principal trends in the development of the method have been fairly completely described in a monograph.[3] At the same time, it has been noted that the mechanism of the epoxidation of olefins by alkyl hydroperoxides and, in particular, the mechanism of the stage involving oxygen transfer to the substrate has not been ultimately elucidated.

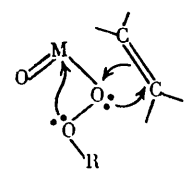
Most investigators have adopted mechanisms involving the formation of the complexes (XIII) and (XIV):[3,124]



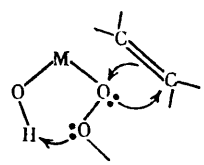
(XIII)



(XIV)



(XV)

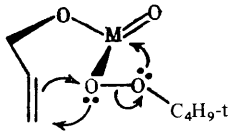


(XVI)

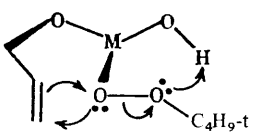
However, this is open to the objection that, according to the structures of compounds (XIII) and (XIV), the internal O(1) oxygen atom and not the more nucleophilic external O(2)

oxygen atom functions as the centre for the coordination with the catalyst in RO(1)O(2)H. This mechanism does not explain the exceptional reactivity of allyl alcohols.[125,126] Having examined the stereochemistry of the oxidation of the latter, Sharpless proposed mechanisms in which compounds (XV) and (XVI) are formed.[125,127] Preliminary experiments with the aid of tracer atoms showed that the ROOH molecule itself and not the peroxy-compound of the catalyst is involved in the stage responsible for the oxygen transfer.[128,129]

All the conditions for the simultaneous coordination of the catalyst to the peroxide oxygen and the allyl hydroxy-group exist in the complexes (XV) and (XVI), while in compounds (XIII) and (XIV) such interaction is ruled out on geometrical grounds:

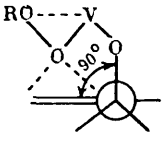


(XV)

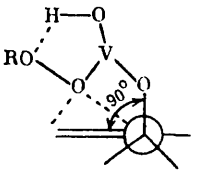


(XVI)

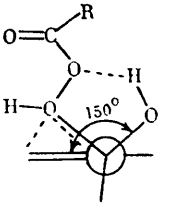
In their study of the stereochemical aspects of the epoxidation of cycloalkenols, Itoh et al.[126] determined the most probable geometry of the transition state when the alkyl hydroperoxides (XV) and (XVI) and the peracids (XVII) are used:



(XV)

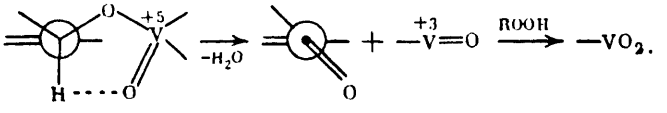


(XVI)



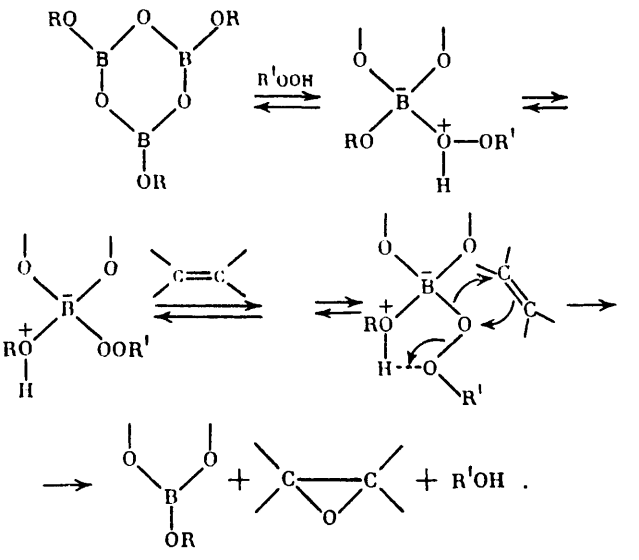
(XVII)

In the case of secondary allyl alcohols with a fixed conformation, which prevents formation of the complexes (XV) and (XVI) with a quasi-axial disposition of the OH group, the oxidation is by the oxygen of oxovanadium with subsequent regeneration of the oxidant by the hydroperoxide:

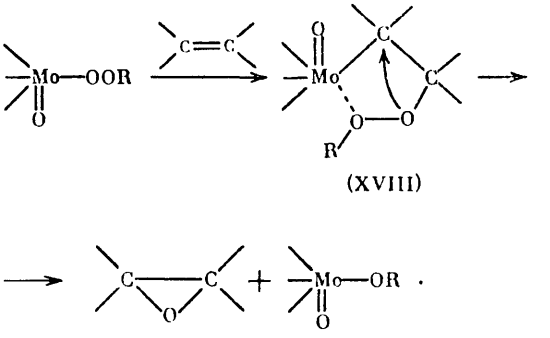


The ability of the metals employed in the oxidation reaction to form three-membered peroxy-compounds [128,129] makes a shift of the central atom from the active oxygen to the alkoxide anion in compound (XV) entirely realistic. Under other acid–base conditions, the "proton" mechanism (XVI), corresponding to the idea of nucleophilic substitution at the peroxide oxygen atom, may be preferable.[55] The relative contributions of the mechanisms (XV) and (XVI) are apparently determined by the ratio of the oxo- and hydroxylated forms of the catalyst.

In the light of the ideas described concerning the role of aprotic and protic acids, epoxidation in the presence of borates[130] can proceed as follows in the peroxide oxygen transfer stage:

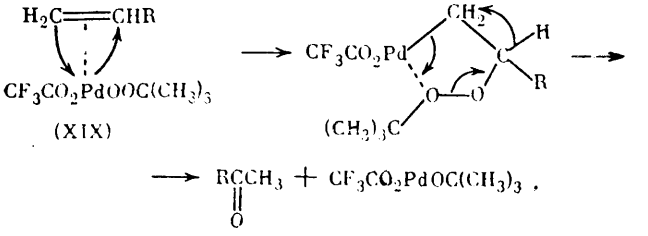


A mechanism has been proposed for the hydroperoxide epoxidation with formation of a five-membered metal peroxide complex (XVIII):[131]



(XVIII)

The above mechanism is based on the analogy with the oxidation of terminal alkenes to methyl ketones by peroxy-compounds of palladium (XIX):



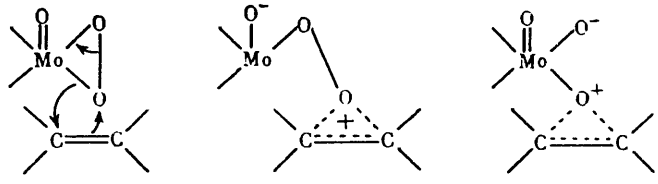
(XIX)

However, the reactions considered are significantly different in their nature. In contrast to molybdenum compounds, palladium compounds form complexes with olefins not only via donor–acceptor interactions but also via a dative interaction and are probably capable of adding to the double bonds. The formation of a C–Pd bond is indicated by the involvement in the reaction of only the terminal double bond, with a sterically accessible carbon atom, and also by the unusual hydride shift§. On the other hand, the formation of Mo–C and V–C

§ In the isomerisation of epoxy-compounds to aldehydes or ketones, the unoccupied orbital accepting the hydride anion arises at the more substituted carbon atom.[57]

bonds is unlikely, while the formation of five-membered complexes analogous to (XVIII) is inconsistent with experimental epoxidation data.[2,132] In particular, the comparable rates of epoxidation of cyclohexene and norbornene (an effective 1,3-dipolarophile)[132] are evidence against the 1,3-dipolar addition to the double bond.

The operation of ionic mechanisms in which compounds (XXI) and (XXII) are formed in organic (non-polar) media appears less probable than the synchronous mechanism involving the formation of compound (XX):



(XX) (XXI) (XXII)

The autoacceleration and inhibition effects, indicating that the competing associative process can promote or conversely hinder the insertion of the alkyl hydroperoxide and then the olefin in the coordination sphere of the catalyst, are characteristic of the alkyl hydroperoxide epoxidation[3] and of a series of heterolytic reactions of hydrogen peroxide and peracids.[55,56]

VII. STEREOSELECTIVITY AND REGIOSELECTIVITY OF THE HYDROPEROXIDE EPOXIDATION

Henbest and Wilson laid the foundations of stereoselective epoxidation having established that the allyl hydroxy-group in cyclohexenol is coordinated to the peracid and promotes *cis*-epoxidation.[133] The rate of reaction is then higher by an order of magnitude than in the case of the corresponding cyclohexenyl acetate.

Alkyl hydroperoxides showed an even greater selectivity in the oxidation of cyclic and saturated alcohols (see Table) in the presence of vanadium and molybdenum compounds.[126, 134–137] 2-Cyclohexanol was oxidised more readily than cyclohexene, while cyclohexene was more reactive when a peracid was employed.[134]

It is striking that the epoxidation of C_6–C_9 cycloalkenols with *m*-chloroperbenzoic acid (MCPBA) is accompanied by a change in the direction of attack by the reagents on passing from a seven-membered to an eight-membered ring (see Table). This finding can be accounted for by the conformational changes arising following an increase in ring size. On the other hand, under the conditions where a vanadium catalyst is used the coordination of the OH group to the central atom is so strong that it alters the conformation and ensures the *syn*-attack by the oxidant. A *syn*-directing influence is also shown by the hydroxy-group in 3-cyclohexenol.[134] In this case the molybdenum catalyst is more effective than the vanadium catalyst.

The most probable geometry of the transition state in the epoxidation of cyclohexenols by peracids and ROOH has been published by Itoh et al.[126] (see Section VI).

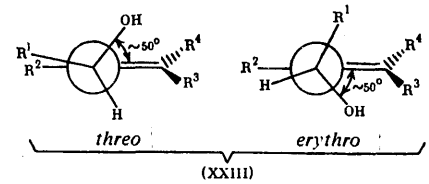
It is of interest to note the highly selective formation of *cis*-epoxyalcohols in the oxidation of cyclenes by atmospheric oxygen in the rpesence of vanadyl acetylacetonate[138] with the intermediate formation of allyl hydroperoxides. The catalytic reaction of the cycloalkenyl hydroperoxides themselves has been investigated[139] (see Table). The exclusive formation of *cis*-epoxyalcohols suggests that the epoxidation is intramolecular.

The directing influence of the hydroxy-group has been used successfully also in the hydroperoxide epoxidation of acyclic systems. A high regioselectivity (84–93%) has been attained in the catalytic epoxidation of geraniol, linalool,[134] and certain analogues of farnesol[140] by t-butyl hydroperoxide (see Table). ROOH epoxidises the allyl 2,3-double bond, while peracids oxidise preferentially the more remote 6,7-double bond.

The possibility of the selective hydroperoxide epoxidation of allyl alcohols of the type of (XXIII) (see Table) has been demonstrated.[136,141]

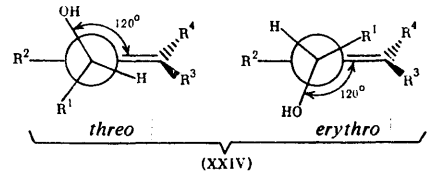
The Table shows that peracids exhibit a high stereoselectivity only for a specific structure of the alkenol (with $R^2 = H$). The presence of a single substituent at the C(3) atom in the *trans*-position lowers the stereoselectivity.[142]

The probable dihedral HO–C–C=C angles in the transition states leading to the *threo*- and *erythro*-isomers in oxidation of (XXIII) by ROOH and of (XXIV) by a peracid have been calculated:[140]



threo *erythro*

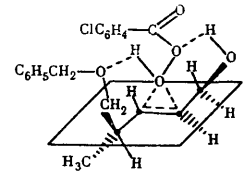
(XXIII)



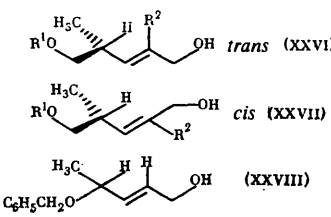
threo *erythro*

(XXIV)

An unusual effect of the joint directing effect of the hydroxy-group and the ester oxygen atom, as in (XXV), has been observed in the epoxidation of the olefinic alcohols (XXVI) and (XXVII), where $R^1 = C_6H_5CH_2$ or H and $R^2 = H$, CH_3 or $Si(CH_3)_3$, by MCPBA.[143,144] The stereoselectivity reaches 86–96%.



(XXV)



trans (XXVI)

cis (XXVII)

(XXVIII)

The high effectiveness of the joint influence of the substituents in the *cis*-isomer is determined, according to the authors,[144] by the geometry of the most stable conformation (XXVII). A similar effect of the functional groups in compound (XXVIII) was not observed.[145]

The directing influence of the bulky trialkysilyl group at the C(2) atom of the alkenol (see Table) is extremely effective.[144–146] In the final epoxyalcohol it can be readily substituted by hydrogen on treatment with $(n\text{-}C_4H_9)_4NF$ in DMF.

Evidently the discovery of the most stable conformation of the alkenol in the ground state and the selection of the corresponding substituents are extremely useful in carrying out the reaction with the expected stereochemical results, although the method,[147] based on the estimation of the relative stabilities of the diastereoisomeric transition compounds in accordance with the Curtin–Hammett principle, is more universal for the prediction of the mode of synthesis.

The stereoselectivity and regioselectivity of the epoxidation of certain substituted alkenes and cycloalkenes.

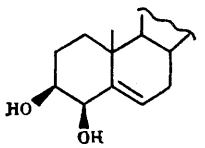
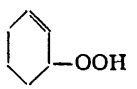
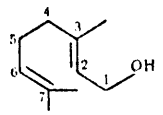
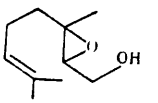
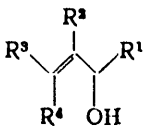
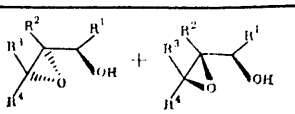
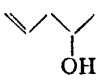
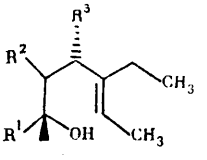
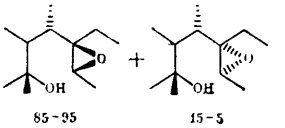
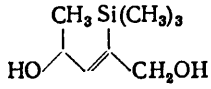
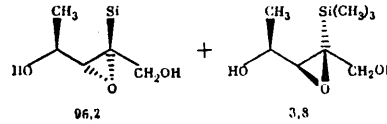
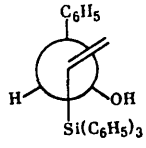
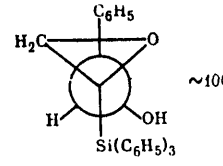
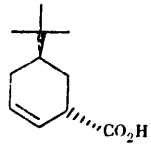
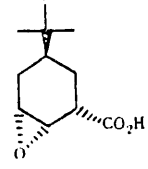
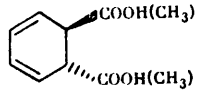
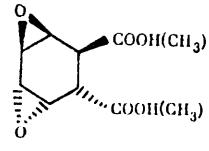
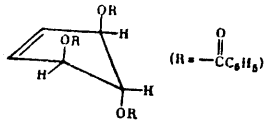
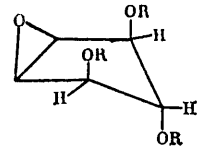
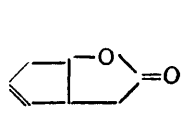
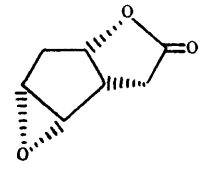
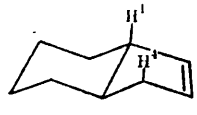
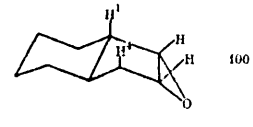
Olefin	Epoxidising agent, catalyst	Content of isomer, %	Refs.
Cyclic aliphatic 5-9-membered *Z*-allyl and 8-20-membered *E*-allyl alcohols, methylenecyclohexenols	t-C_4H_9OOH, $VO(acac)_2$ or $Mo(CO)_6$	*cis*-epoxyalcohols, 91-99	[126, 135, 136]
2-Cyclohexenol 2-Cycloheptenol 2-Cyclo-octenol 2-Cyclononenol	MCPBA ditto » »	*cis*-epoxyalcohol, 95 ditto , 61 » , 0.2 » , 0.2	[126, 133, 135]
3-Cyclohexenol	t-C_4H_9OOH, $Mo(CO)_6$	*cis*-epoxyalcohol, 90	[134]
 4β-Hydroxycholesterol	t-C_4H_9OOH, $VO(acac)_2$ MCPBA	*cis*-epoxyalcohol, 100 *cis*-epoxyalcohol, 66	[134]
	$VO(acac)_2$	*cis*-epoxyalcohol, 100 (yield 79%)	[139]
 Geraniol	t-C_4H_9OOH, $VO(acac)_2$	 93	[134]
 R^2=H; R^3=R^4=H (XXIII)		 *R*R*(erythro)* *R*S*(threo)*	[136, 141]
	t-C_4H_9OOH, $VO(acac)_2$	14 86	
	t-C_4H_9OOH, $Mo(CO)_6$	5 95	
	MCPBA	5 95	
	t-C_4H_9OOH, $VO(acac)_2$	95 5	
	t-C_4H_9OOH, $Mo(CO)_6$	84 16	
	MCPBA	55 45	
	p-NO_2PBA	68 32	
 Pent-4-en-2-ol	t-C_4H_9OOH, $VO(acac)_2$ MCPBA	66 34 55 45	[148, 149]
 Ditto	t-C_4H_9OOH, $VO(acac)_2$ MCPBA	 85-95 15-5 non-stereoselectively	[150]

Table (contd.)

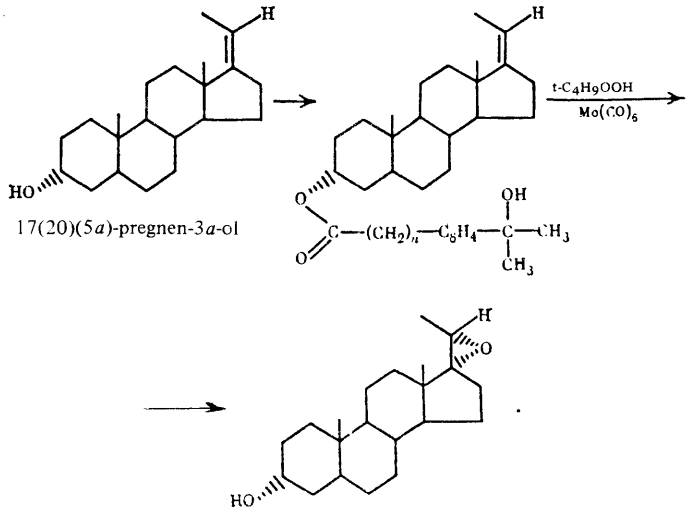
Olefin	Epoxidising agent, catalyst	Content of isomer, %	Refs.
	MCPBA	 96,2 3,8	[145]
	MCPBA	 ~100	[146]
	MCPBA, or CH_3CO_3H, or polymeric peracids in inert solvents	 77-79	[154]
	MCPBA	 ~100	[155]
	CF_3CO_3H	 ~100	[159]
	CH_3CO_3H in HAc	 89	[160]
Ditto	MCPBA in hexane	Ditto, 80	
»	MCPBA in CCl_4	Ditto, 40	
	*p*-NO_2PBA	 100	[161]

Estimation of the strain induced by the interaction of the substituents in the 1-, 2-, and 3-positions in the allyl alcohol makes it possible to predict the structure of the optimum transition state and the result of the reaction as a whole, which has been demonstrated for a series of examples described in the literature.

The stereochemical course of the epoxidation reactions of acyclic 3- and 4-alkenols has been investigated only for individual examples (see Table). Thus pent-4-en-2-ol exhibits only a weak 1,3-asymmetric induction in its reactions with various oxidants,[148,149] while 4-alkenols are epoxidised by t-C_4H_9OOH with a high stereoselectivity (1,4-asymmetric induction).[150]

The stereospecific epoxidation of the olefin bond in steroids[151] and acyclic polyenes[152] has been carried out making use of the influence of a very remote OH group. For this purpose, it was acylated by a hydroxylated reagent (template). The size and geometry of the template enabled

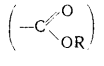
the OH group present in it to cooperate with the oxidant:



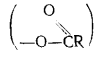
The asymmetric epoxidation of allyl alcohols by alkyl hydroperoxides has been carried out in the presence of vanadium and molybdenum complexes incorporating chiral ligands: hydroxamic acids[127] and *N*-alkylephedrin.[153] The asymmetric induction reached 50%.

The influence of other functional groups on the stereoselectivity of the epoxidation has also been investigated (see Table). The epoxidation of certain βγ-unsaturated acids of the cyclohexene series by peracids has been studied.[154] The tendency towards *cis*-epoxidation relative to the carboxy-group (54–79%) has been observed in inert solvents. The methyl esters of the above acids are epoxidised independently of the medium with the preferential formation of the *trans*-isomers (60–64%). The oxidation of *trans*-1,2-dihydrophthalic acid by MCPBA leads exclusively to mono- and di-epoxides with the *cis*-disposition of neighbouring epoxy- and carboxy-groups even in a weakly basic solvent—ethyl acetate.[155]

The presence of the carboxylate



or acyloxy-group

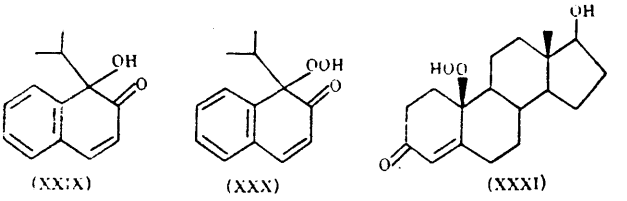


in the ring usually leads to the *trans*-orientation of the oxidant.[133,154,156,157] Nevertheless, when such substituents accumulate, for example, in the case of dimethyl *trans*-1,2-dihydrophthalate[158] or the tribenzoate of cyclopentenetriol,[159] a specific *syn*-directing influence is manifested (see Table).

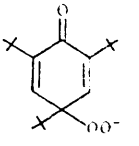
It has been established that the stereochemistry of the epoxidation of the lactone of 2-hydroxy-4-pentenylacetic acid by peracetic acid depends significantly on the nature of the solvent, indicating a relation between the conformation of the molecule and the conditions governing the solvation of the functional group.[160] The mode of epoxidation of unsaturated rings of moderate size does not exhibit a definite dependence on the orientation of the epoxy-group present in them.[161–163]

Dynamic conformational analysis of the epoxidation of substituted five-, six- and seven-membered cyclic olefins and certain bicyclenes[164] showed that the direction of attack by the reagent involving the least conformational distortions predominates. The principles developed in the last study quoted can be used in the planning of a stereospecific synthesis.

The stereoselective synthesis of epoxides from chalcones and naphthoquinones has been carried out with the aid of alkaline hydrogen peroxide or ROOH.[165–168] The use of chiral quaternary ammonium salts based on quinine and quinidine as phase-transfer catalysts made it possible to achieve an excess of one of the enatiomers to the extent of 25–55%. The epoxidation of 1-hydroxy-1-isopropylnaphthalen-2(1*H*)-one (XXIX) with alkaline hydrogen peroxide[169] takes place exclusively in the *trans*-position relative to the hydroxy-group. On the other hand, the intramolecular oxidation of the multiple bond in compounds (XXX),[170] (XXXI),[171] and (XXXII)[172] leads to *cis*-epoxyalcohols:



(XXIX) (XXX) (XXXI)

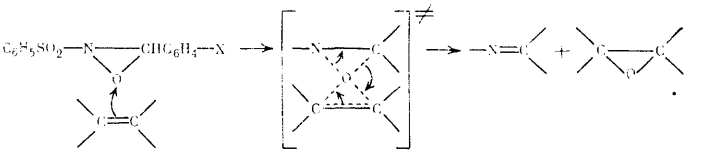


(XXXII)

A rigorously selective intramolecular epoxidation of the multiple 14,15-bond occurred in peracids derived from polyenoic acids: eicosa-*cis*-5,8,11,14-tetraenoic and eicosa-*cis*-8,11,14-trienoic acids.[173] The intramolecular oxidation of hydroperoxides obtained from certain orthoesters and ketals[113] by the method described in Ref. 112 takes place with the olefin double bond much less remote from the peroxide oxygen.

VIII. OXAZIRIDINES AND HETEROCYCLIC EPOXIDISING INTERMEDIATES

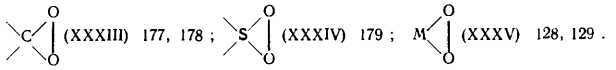
Oxaziridines containing electron-accepting substituents are capable of oxidising sulphides, amines, organometallic compounds, and olefins:[174]



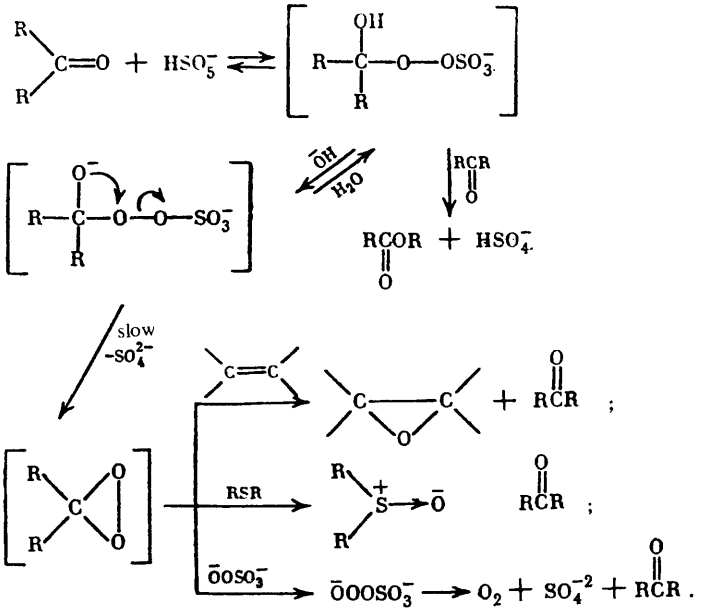
For example, *trans*-stilbene is epoxidised by 2-arenesulponyl-3-aryloxaziridines at 60 °C in the course of 10–12 h with a 95% yield of the epoxide¶.

¶ For comparison, one may note that under severe conditions oxirans are capable of transferring oxygen to phosphines (150 °C),[175] while sulphur dioxide can transfer oxygen to ethylene (400 °C).[176]

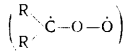
In certain reactions involving peroxy-compounds, ozone, or singlet oxygen, the formation of highly reactive intermediates (XXIII) and (XXIV), resembling an oxaziridine, has been postulated:



The peroxy-compounds of certain transition metals (XXXV) have been isolated and investigated as epoxidising agents. The formation of the dioxiran (XXIII) has been suggested in the decomposition of potassium peroxymonosulphate (potassium Caroate—$KHSO_5$) in the presence of a ketone: [177]



In water at pH 7.5 and a temperature of 2–10 °C the dioxiran epoxidises, also in the absence of a ketone, αβ-unsaturated ketones, acids, and their esters (which cannot be oxidised either by peracids or potassium Caroate) as well as the usual olefins. The Baeyer–Villiger reaction takes place at a negligible rate under these conditions. The reaction is rigorously stereospecific, which rules out the involvement of the carbonyl oxide

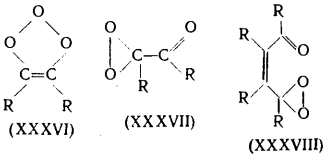


in it.

As a very powerful oxidant, the dioxiran can transfer active oxygen to the peracid anion with the subsequent formation of singlet oxygen. The rate of decomposition of the peroxymonosulphate anion is described by the equation [180]

$$W = k\cdot[HSO_5^-]\,[\text{ketone}]\,[\bar{O}H].$$

It has been suggested that the ozonisation of alkynes [178,181] results in the formation, together with peracids, of the epoxidising intermediates (XXXVI) and (XXXVII), the dioxiran (XXXVII) oxidising alkenes non-stereospecifically:

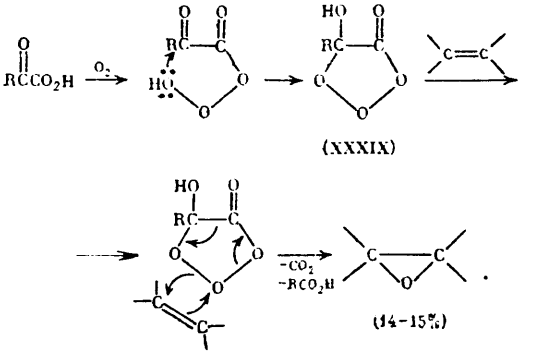


Compounds (XXXVI) and (XXXVII) are extremely reactive and epoxidise olefins at −70° and −25 °C respectively.

The dioxiran (XXXVIII) is regarded as an intermediate which transfers oxygen in the epoxidation of tetramethylethylene to the endoperoxides of furan and its derivatives. [182]

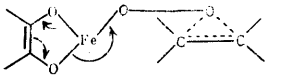
The sulphur-containing analogue of dioxiran (XXXIV) or its isomer sulphenyl oxide ($S=\dot{O}-\bar{O}$) is formed, according to Martin and Martin, [179] under the conditions of the oxidation of a compound of tetracovalent sulphur by hydrogen peroxide in the presence of cyclohexene or norbornene at −78 °C. An increase of temperature to room temperature completes the epoxidation reaction.

The oxidative decarboxylation of α-ketoacids with the aid of singlet oxygen, which proceeds via the trioxolan (XXXIX) capable of transferring oxygen to olefins, including tetracyanoethylene, in the temperature range from −100° to −150 °C, has been described: [183]

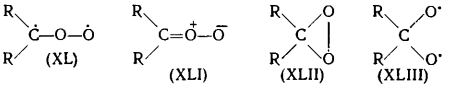


IX. THE OXENOID MECHANISM. CARBONYL OXIDE AND ITS ANALOGUES

By analogy with carbenoid, the term oxenoid is applied to the kinetically unstable species capable of transferring oxygen with a sextet of electrons to the substrate and of being converted into a neutral molecule. In his study of the enzymic oxidation of olefins by molecular oxygen, [184] Hamilton proposed the "enediol–Fe–O_2" oxenoid model, which transfers oxygen to the substrate:



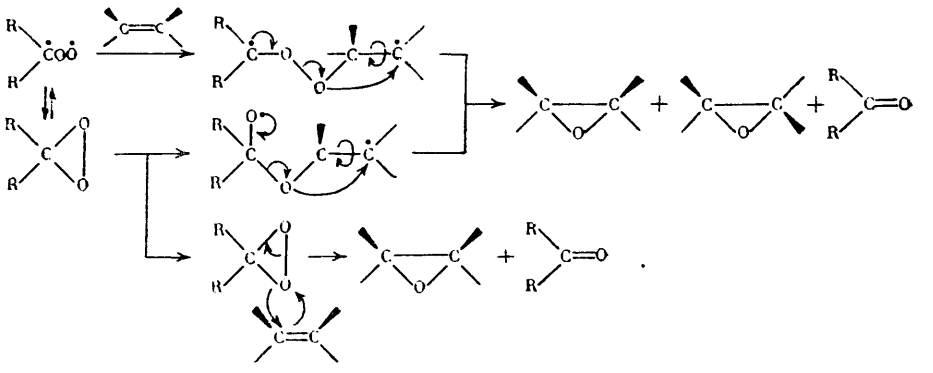
However, it has been suggested [185] that the consumption of peroxide in such systems proceeds via a radical chain mechanism. The "carbonyl oxide" (XL) or (XLI) (the Criegee intermediate) is a typical oxenoid. The dioxiran (XLII) and "methylene dioxide" (XLIII) are isomers of compound (XL): [178, 186–188]



Quantum-chemical calculation has shown that, as regards energy, the dioxiran is more favourable by 33.7–36 kcal than carbonyl oxide and by 15 kcal than methylene dioxide. [189,190]

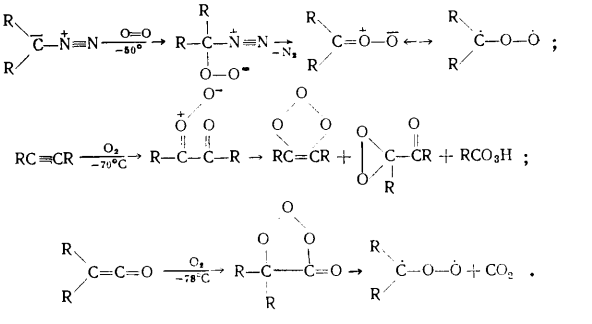
The oxenoid mechanism presupposes the involvement of any of the species indicated in the epoxidation reaction. One cannot rule out the possibility that the olefin can induce the homolytic rupture of the bonds in compound (XLII), abolishing the results of the interaction of olefins with compound (XL), (XLII), and (XLIII).

The epoxidation of olefins by carbonyl oxide and its isomers allows the formation of a biradical intermediate and rotation about the σ-bond: [186,187,191]



This mechanism is supported by the partial stereospecificity of the reaction. For example, *trans*-hex-3-ene gives rise to 99% of the *trans*-epoxide and 1% of the *cis*-isomer, while *cis*-hex-3-ene produces 95% of the *cis*-epoxide and 5% of the *trans*-isomer.

Carbonyl oxide is formed when diazomethane is treated with singlet oxygen[186] and when acetylenes,[178] ketenes,[187,188] and olefins[191] are ozonised:



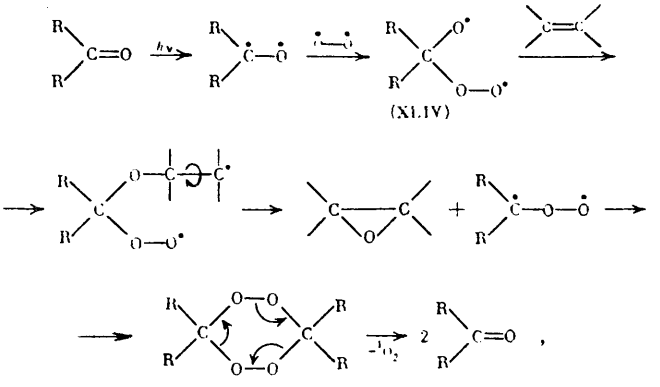
The ozonisation of olefins is known to lead to the formation of ozonides—the products of the coupling of Criegee intermediates with a carbonyl compound. However, in the presence of tetracyanoethylene, which is an effective 1,3-dipolarophile and which is not ozonised at a low temperature (−78 °C), epoxytetracyanoethane is formed in a quantitative yield.[192] Tetramethylethylene and norbornene are not epoxidised under these conditions.

It follows from the study of Gillies[191] that other electron-deficient olefins, namely symmetrically fluorinated ethylenes, can be epoxidised by carbonyl oxides. Ozonolysis of perfluoro- and 1,2-difluoro-ethylenes differs from that of the geminal difluoro-olefins and the usual alkenes. The study of the deuteriated substrates showed that the reaction takes place with partial cleavage of the olefin and with attack by fluorocarbonyl oxide on the olefin.

Evidently the introduction of an electron-accepting substituent into carbonyl oxide weakens its nucleophilic properties and its ability to attack the carbonyl group, permitting an electrophilic attack on the olefin.

By analogy with the dioxiran (XXXVII), the trioxides (XXXVI) and (XXXIX) and the sulphenyl oxide (XXXIV), mentioned above, may be included among oxenoid oxygen transferring agents.

The biradical (XLIV), formed as an intermediate in the photochemical oxidation of many cyclic and acyclic olefins sensitised by aliphate α-diketones or benzophenone, is also regarded as a probable epoxidising agent:[193]

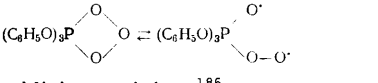


(XLIV)

Regardless of the geometry of the initial olefin, only the *trans*-epoxide is formed in the reaction. Benzophenone is then hardly consumed and, despite a fivefold excess of the olefin, a high yield of the oxiran is ensured.

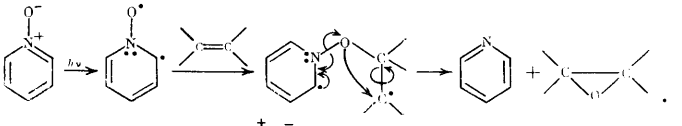
One should note that certain related photochemical epoxidation reactions in the presence of benzoin[194] and α-ketoacids[195] have been explained by the epoxidising action of acylperoxy-radicals. In this case the sensitisers are consumed as reactants.

The analogue (XLIV), which is a triphenylphosphite ozonoid,



exhibits a weak epoxidising activity.[186]

The *N*-oxides of nitrogen-containing heterocycles,[196,197] idosobenzene,[198] and phenylbenozyldiazomethane (azibenzil) are oxenoid reagents in the presence of oxygen.[199] Oxygen transfer to olefins by the *N*-oxide takes place under the conditions of photolysis at −70 °C and is characterised by the absence of stereo specificity: a *cis*-olefin gives rise to a 1:1 mixture of the *cis*- and *trans*-epoxides. Preliminary isomerisation of the *N*-oxides to oxaziridines is ruled out, because the latter epoxidise olefins stereospecifically.[176] The epoxidation mechanism can be accounted for if the *N*-oxide fragment $-C=\overset{+}{N}-\bar{O}$ is regarded as a heteroanalogue of carbonyl oxide:



Iodosobenzene ($C_6H_5-\overset{+}{I}-\bar{O}$) epoxidises and hydroxylates hydrocarbons in the presence of catalysts: iron αβγδ-tetraphenylporphyrinate and chlorodimethylferriprotoporphyrin. The system is very sensitive to the structure of the olefin

and the catalyst ligands. It has been suggested that iodosobenzene transfers oxygen to the substrate via a "catalyst–oxygen" intermediate.

A complex epoxidising olefins is formed from azilbenzil $C_6H_5COC(N_2)C_6H_5$ on interaction with oxygen in the presence of palladium acetate. The reaction with *cis*-olefins loses its stereoepcificity. It is believed[199] that the catalyst accelerates the decomposition of azibenzil and promotes the formation of a ketocarbene–oxygen complex, which plays the role of oxenoid.

The action of an alkaline solution of xenon trioxide and sodium perxenate (Na_4XeO_6) on an olefin has been investigated.[200,201] In contrast to certain inorganic oxides (OsO_4, MnO_4^-), which induce *cis*-1,2-hydroxylation, XeO_3 produces only epoxides, like peroxide reagents.

The ratio of the rates of epoxidation of norbornene and cyclohexene is small (2.4–2.7) and is evidence against a five-membered transition state characteristic of 1,3-dipolar addition.

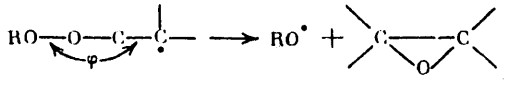
At the same time the weak stereospecificity of the reaction rules out the possibility of the operation of a typical synchronous mechanism with a three-membered transition state. The reaction apparently proceeds via the oxenoid mechanism involving the formation of a weakly bound bridged three-membered complex, permitting homolytic ring opening and rotation about the σ-bond.

X. SOME ASPECTS OF RADICAL EPOXIDATION

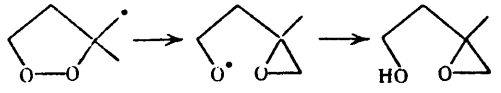
The epoxidation of olefins by alkyl- and acyl-peroxy-radicals has been described in a review.[122] Reaction of this type are non-stereospecific, which indicates a multistage mechanism of the formation of the ring. According to Sawaki and Ogata,[194] the *trans*-selectivity of the epoxidation by acylperoxy-radicals follows from the relative stabilities of the two possible transition states in the epoxide ring closure stage—the state with the transoid disposition of the bulkiest substituents is preferable.

The radical adduct $(CH_3)_2\overset{\vdots}{N}{-}O{-}O^{\cdot}$, formed in the epoxidation of many olefins by oxygen in the presence of amines and a Lewis acid ($ZnCl_2$), has been considered as an analogue of an acyl peroxy-radical.[202] Under the influence of the amine, the oxirans are converted into aminoalcohols under the conditions of the synthesis, although in the case of cyclooctene the intermediate oxiran was isolated.

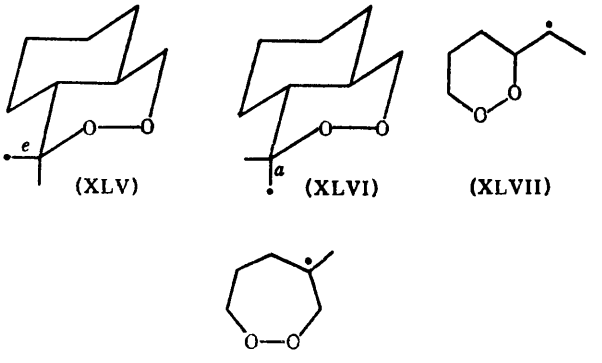
Important data about the stereochemistry of the epoxide ring closure in peroxyalkyl radicals have been published.[203,204] It has been shown that an angle close to 180° between the bonds of the leaving alkoxy-radical and the attacking carbon atom carrying the unpaired electron is a condition for the homolytic substitution at the peroxide oxygen atom (S_H):



Thus the formation of epoxyalcohols in accordance with the scheme



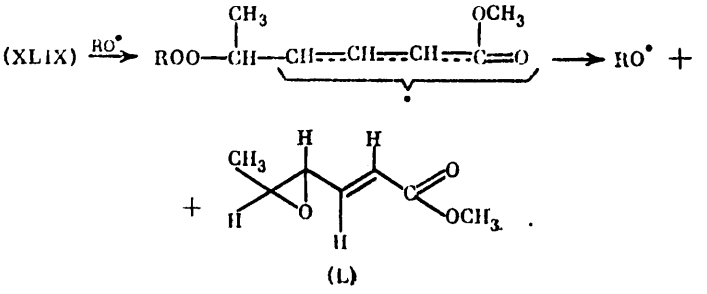
has been observed only in the radicals (XLV) and (XLVII) and not in their analogues (XLVI) and (XLVIII):



(XLV) (XLVI) (XLVII)

(XLVIII)

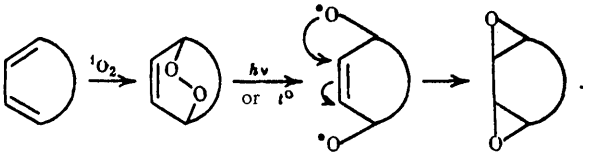
In contrast to the typical non-stereospecific epoxidation of olefins by alkyl- and acyl-peroxy-radicals, conjugated dienones and diene esters are epoxidised by molecular oxygen strictly stereo- and regio-selectively at the γδ-double bond.[205] For example, methyl sorbate (XLIX) forms exclusively the *E*, *E*-epoxide (L):



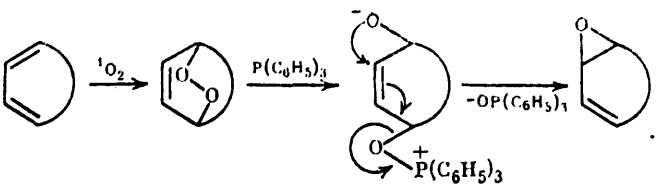
(L)

The stereospecific free-radical epoxidation of 7,8-dihydroxy-7,8-dihydrobenzo[*a*]pyrene by the hydroperoxides of polyunsaturated aliphatic acids has been noted.[206]

In the synthesis of bisepoxides from cyclic 1,3-dienes, the method used involved the oxygenation of the latter compounds by singlet oxygen with subsequent photochemical or thermal isomerisation of the resulting *endo*-peroxides:[207]



This entails the exclusive formation of *cis*-diepoxides. The deoxygenation of the *endo*-peroxide by triphenylphosphine leads to monoepoxides:

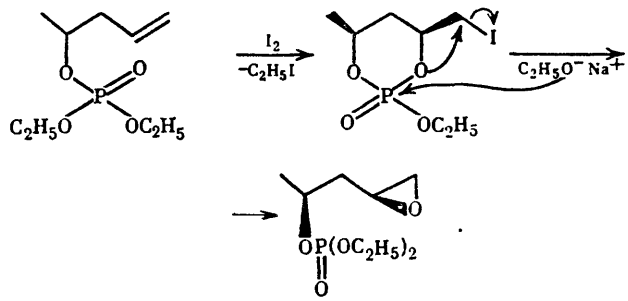


Combination of the above methods with the methods for the oxidation of olefins with the aid of peracids and via halogenohydrins gives rise to the possibility of the specific synthesis of di-, tri-, and poly-epoxides from hepta and octa-trienes

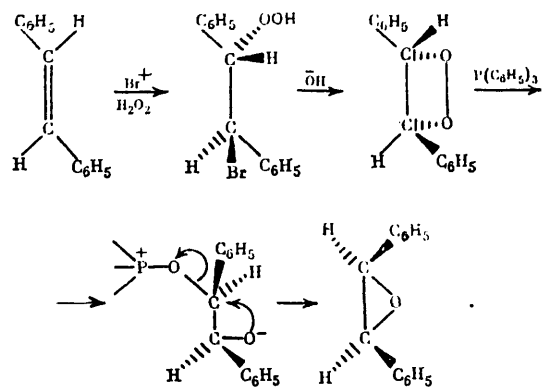
as well as other cyclic polyenes.[162,163,208] The strained system of the cyclopentadiene *endo*-peroxide gives rise to many side products on thermolysis (epoxyketones, ketoalcohols, and others).[209] On the other hand, in the case of substituted cyclopentadienes the yield of diepoxides is much higher.

XI. THE SYNTHESIS OF OXIRANS BASED ON INTRAMOLECULAR NUCLEOPHILIC SUBSTITUTION

A number of methods for the stereospecific synthesis of oxirans have been proposed. Bartlett and Jernstedt[148] achieved a highly stereoselective epoxidation of 3-alkenols by the iodination of the corresponding phosphates:[148]

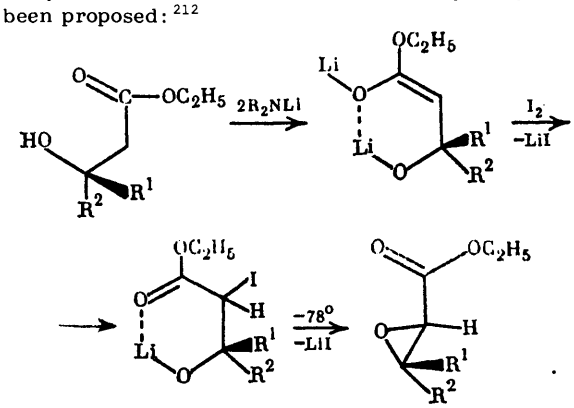


A stereoselective conversion of *trans*-stilbene into the *cis*-epoxide with a threefold inversion of the substrate[209] has been achieved via the deoxygenation of dioxetan with triphenylphosphine:



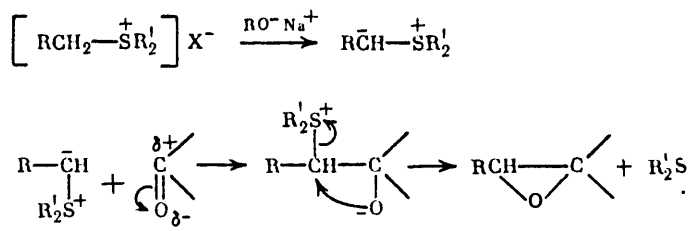
The deoxygenation of cyclo-1,3-diene *endo*-peroxides takes place similarly in the presence of triphenylphosphine.[207] The halogenoactonisation procedure has been used for the epoxidation of unsaturated acids[210] and alcohols:[211]

A new method for the stereoselective synthesis of αβ-epoxyesters by the oxidation of the dianions of β-hydroxyesters has been proposed:[212]



The high degree of asymmetric induction in such syntheses is due to the conformational features of the intermediate cyclic complexes, which make one of the pathways to the electrophilic addition to the double bond preferable.

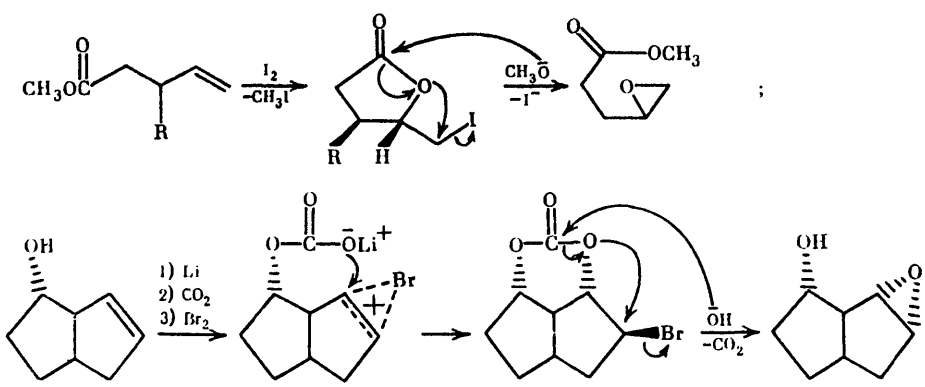
The method of synthesis of oxirans based on the coupling of sulphonium ylides to oxo-compounds has been described in several reports:[213–215]

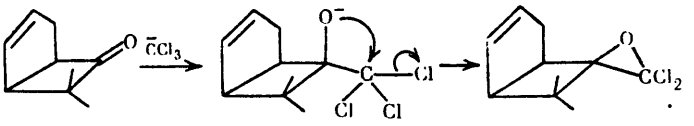


An alkyl phenyl sulphide can be the leaving group in an alkaline medium in the presence of a hydroxy-group in the α-position,[91] which has been used in the synthesis of an optically active epoxide–disparlure.

A series of new syntheses, in which the epoxide ring is closed by the Darzens method have been described, for example, the epoxyannelation of the carbanions of β-ketoesters and β-diketones to 1,4-dichlorobutan-2-one[216] and the condensation of α-mercaptocarbonyl compounds with 2-chloroacrylonitrile in the presence of tetraalkylammonium iodide as the catalyst.[217]

Under the conditions where a phase-transfer catalyst is used, dichloroepoxides, which readily rearrange to the chlorides of carboxylic chloroacids, have been obtained from ketones and chloroform in an alkaline medium:[218]





The epoxidation of styrene and cyclohexene by sodium hypochlorite, catalysed by transition metal complexes in the presence of a phase-transfer catalyst, has been described.[219]

Oxirans can be obtained from vicinal diols by treating the latter with an equimolecular amount of tosyl chloride and powdered sodium hydroxide.[220] The epoxide ring is reduced after the tosylation of one hydroxy-group.

The C_2–C_{18} alkane-1,2-diols are dehydrated with formation of epoxides also in the gas or liquid phase at 250–550 °C in the presence of basic catalysts (AcONa, $Na_2B_4O_7$, Na_3PO_4, etc.).[221] The thermolysis of chlorohydrin esters at 150–250 °C in the presence of catalysts (ammonium of phosphonium salts) leads to the same result.[222]

The survey of the literature data makes it possible to differentiate five types of mechanisms of the epoxidation of olefins.

The first type includes many-centre synchronous mechanisms of the transfer of oxygen by the peroxide reagent to the substrate, which are completely stereospecific.[56,125,126,143] The synchronous mechanism is characteristic of many instances of hydroperoxide oxidation in the presence of protic or aprotic acids and bases whose composition constantly varies during the reaction. The competing associated processes taking place in such systems, in particular the non-equilibrium solvation of the reactants, exert a major influence on the rate and direction of the chemical reactions, producing a number of kinetic effects: autocatalysis, inhibition, dependence of the specific rate (k) and the activation parameters on the concentrations of the reactants and acid–base associated species, etc.

The second type involves an ionic mechanism which operates in the epoxidation of polar olefin bonds by hydrogen peroxide or alkyl hydroperoxides in an alkaline medium.[56,83,166] In the aliphatic series, *trans*-selectivity due to the rotation about the C–C bond in the intermediate carbanion, is observed.

The next type involves a radical asynchronous mechanism, presupposing the formation of a monoradical[122] or biradical[186,193,196] intermediate complex whose life span is sufficient for the inversion of the configuration of the initial olefin. A conformational equilibrium, mainly in favour of the *trans*-isomer of the oxiran, is then established, which renders the reaction non-stereospecific. An exceptional case of *cis*-selectivity has been described.[223]

Stereospecific radical epoxidation also occurs.[122,205]

Reactions whose mechanism is based on the nucleophilic closure of the epoxide ring constitute a separate group. The following are the usual leaving groups: Hal,[148,211,218] SR_2,[213,214] and OH.[220,221] The electrochemical epoxidation can be included in the same type.[224,225]

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The Chemistry of Organic Compounds Containing the Thiodiimide Group

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Data on the methods of synthesis, the electronic and steric structures, and reactivities of organic compounds containing the thiodiimide group—N=S=N—are surveyed.
The bibliography includes 172 references.

CONTENTS

I. Introduction 1006
II. Synthesis 1006
III. Geometry and electronic structure 1010
IV. Chemical properties 1016

I. INTRODUCTION

Heterocumulenes containing a quadrivalent dicoordinate sulphur atom are highly reactive and have unusual steric and electronic structures.[1] Among them, substances whose molecules incorporate the thiodiimide group $-N=S=N-$† are of special interest from both the theoretical and practical standpoints. Apart from the synthetic possibilities arising from these substances, the increased interest in them is associated with the fact that they can be regarded as the simplest oligomeric analogues of the polymeric sulphur nitride $(SN)_x$[2]— a molecular metal and superconductor.[3,4] The informal character of the analogy is confirmed by the electrophysical properties of certain thiodiimides. In particular, poly(arylene thiodiimides) $(-Ar-N=S=N-)_n$ are semiconductors and exhibit photoconduction with a spectral sensitivity extending to the near infrared,[5,6] while a series of low-molecular-weight thiodiimides can be used as highly sensitive pigments in electrophotographic processes and in the generation of an image by means of photoelectrophoresis.[7]

The present review examines critically and gives a systematic account of the available information about the methods of synthesis, structure, and reactivity of open-chain compounds in which the thiodiimide group is linked to two organic or organoelemental moieties. Whenever possible, a comparison is made with the polymeric sulphur nitride $(SN)_x$. Heterocyclic compounds containing the $-N=S=N-$ group, such as 2,1,3-thiadiazole and its derivatives, naphthol[1,8-*c*,*d*]-1,2,6-thiadiazine, etc., are not given special considerations. Studies on the coordination chemistry of organic thiodiimides, a review of which has been published recently,[8] are not examined either.

During the preparation of the review for the press, a survey of the chemistry of aza-analogues of sulphur dioxides, including thiodiimides, was published.[9] The present review was written from a somewhat different standpoint and is of a more specialist character, so that these two publications do not overlap but rather supplement one another.

†The $-N=S=N-$ group does not have a generally accepted name in Soviet literature. We prefer to refer to it as the thiodiimide group following the authors of the following monograph: S.N.Borisov, M.G.Voronkov, and E.Lukevics, "Kremneorganicheskie Proizvoidnye Fosfora i Sery" (Organosilicon Derivatives of Phosphorus and Sulphur), Izd.Khimiya, Leningrad, 1968, p.202.

II. SYNTHESIS

Organic compounds containing the thiodiimide group can be synthesised from primary amines and elemental sulphur under conditions of the Pishchimuka reaction. However, this simplest reaction is one of the least investigated.

The most general method of synthesis of the compounds considered involves the interaction of primary amines with the halides of bivalent or quadrivalent sulphur or with *SS*-dihalogenosulphimines, which can be regarded as monoimino-derivatives of quadrivalent sulphur halides. Another general method of synthesis of thiodiimides involves the condensation of *N*-sulphinylamines or *N*-sulphinylamides. This procedure is partly related to the first group of reactions by the fact that *N*-sulphinylarylamines are the starting materials for the synthesis of *N*-aryl-*SS*-dichlorosulphimines.[10]

The third group of reactions, which lead to organic thiodiimides, are those of *NN*-dichloroamides with dichloromono- and dichlorodi-sulphanes, elemental sulphur, or *SS*-dichlorosulphimines, as well as the reactions of *N*-chlorobenzamides with sulphur. It may be[11,12] that these reactions proceed via the intermediate formation of thionitroso-compounds[13] or their dimers.

Sulphur nitride $(SN)_4$ and trithiazyl trichloride $(NSCl)_3$, whose synthetic possibilities have not apparently been as yet exhausted, serve as interesting sources of sulphur–nitrogen fragments for organic thiodiimides. The same compounds also function as starting materials in the synthesis of the polymeric sulphur nitrides $(SN)_x$.[3,4,14]

1. *NN*-Dialkylthiodiimides

NN'-Dialkylthiodiimides are obtained by the reaction of aliphatic amines with sulphur tetrahalides (or their monoimino-derivatives)[15-22] or with dichloromonosulphane.[18,23] They are also formed on thermolysis of *N*-thiosulphinyl-alkylamines[24] and on reaction of *N*-halogenoalkylamines with bis-(dimethylamino)-sulphane.[25] αα'-Bis(dialkylamino)-ααα'α'-tetrachloro-substituted thiodiimides are formed on interaction of cyanomides with dichloromonosulphane:[26]

$$AlkNH_2-\left[\begin{array}{l}\xrightarrow[-HX]{SX_4} AlkN=SX_2 \xrightarrow[-HX]{AlkNH_2}\\ \xrightarrow[-HX]{SCl_2} (AlkNS)_x \xrightarrow[-S]{\Delta}\end{array}\right] \rightarrow (AlkN=)_2S;$$

$X = Cl, F;$

$$t\text{-}BuN=S=S \xrightarrow[-S]{\Delta} (t\text{-}BuN=)_2S;$$

$$Alk_2N-CN \xrightarrow[-S_2Cl_2]{SCl_2} (Alk_2N-CCl_2-N=)_2S\ .$$

Bis(perfluoroalkyl)thiodiimides have been synthesised from *SS*-dichloro-*N*-polyfluoroalkylsulphimines and trifluoromethylamine and its *NN*-dichloro-derivative.[27] In addition, *N*-heptafluoroisopropyl-*N'*-heptafluoroisopropylsulphenyl- and bis(heptafluoroisopropylsulphenyl)-thiodiimides are formed in low yields on interaction of thiazyl fluoride NSF with perfluoropropene.[28]

2. *NN'*-Bis(trimethylsilyl)thiodiimide and Related Compounds

NN'-Bis(trimethylsilyl)thiodiimide is formed on interaction of sodium *NN*-bis(trimethylsilyl)amide with thionyl chloride,[29] sulphur dioxide, or dichloromonosulphane[30] and also on interaction of trithiazyl trichloride with hexamethyldisilazane:[31]

$$\left.\begin{array}{l}(Me_3Si)_2NNa \xrightarrow{SOCl_2,\ SO_2\ \text{or}\ SCl_2} \\ (Me_3Si)_2NH \xrightarrow[-HCl]{(NSCl)_3}\end{array}\right\rangle \longrightarrow (Me_3SiN{=})_2S\,.$$

The reaction between trithiazyl trichloride and the corresponding tertiary amines is a more general process, which makes it possible to obtain bis(trimethylgermyl)- bis(trimethylstannyl)-, and bis(trimethylplumbyl)-thiodiimides in addition to the bis(trimethylsilyl) derivatives:[32]

$$(Me_3M)_3N \xrightarrow[-Me_3MCl]{(NSCl)_3} (Me_3MN{=})_2S\ ;$$
$$M = Si,\ Ge,\ Sn,\ Pb\,.$$

A group of monosilylated thiodiimides have been obtained by the single-stage reaction of *N*-sulphinylamines with lithium *NN*-bis(trimethylsilyl)amide,[33] while *N*-t-butyl-*N'*-trimethylsilylthiodiimide has been obtained by the reaction of *N*-sulphinyl-trimethylsilylamine with lithium t-butyldiorganylfluorosilylamides.[34] The latter substance has also been synthesised from *N*-t-butyl-*SS*-dichlorosulphimine and lithium *NN*-bis(trimethylsily)amide:[135]

$$(Me_3Si)_2NLi \left\langle \begin{array}{l} \xrightarrow{RNSO} R{-}N{=}S{=}N{-}SiMe_3\ ; \\ \xrightarrow[-LiCl;\ -Me_3SiCl]{t\text{-}BuN{=}SCl_2} t\text{-}Bu{-}N{=}S{=}N{-}SiMe_3\ ; \end{array}\right.$$
$$R = Et,\ t\text{-}Bu,\ Ph,$$
$$t\text{-}BuNLi \xrightarrow[-LiF;\ -1/n(-SiR_2O-)_n]{Me_3SiNSO} t\text{-}Bu{-}N{=}S{=}N{-}SiMe_3\,.$$
$$\quad |$$
$$\quad R_2SiF$$

N-Heptafluoroisopropyl-*N'*-trimethylsilylthiodiimide has been obtained from *N*-sulphinylheptafluoroisopropylamine and $(Me_3SiN{=})_2S$.[36]

A general procedure, consisting of the interaction of equimolar amounts of bis(trimethylsilyl)thiodiimide with arenesulphenyl chlorides, has been proposed for the synthesis of *N*-arenesulphenyl-*N'*-trimethylsilylthiodiimides:[2]

$$(Me_3SiN{=})_2S \xrightarrow[-Me_3SiCl]{ArSCl} Ar{-}S{-}N{=}S{=}N{-}SiMe_3\,.$$

N-Pentafluorobenzenesulphenyl-*N'*-trimethylsilylthiodiimide has been obtained from trithiazyl trichloride and *N*-pentafluorobenzenesulphenyl-*N*-trimethylsilylamine.[31]

Monosilylated thiodiimides are also formed in the reaction of sulphur nitride $(SN)_4$ with *N*-trimethylsilyl-substituted secondary alkylamines.[37] Bis(trimethylstannyl)thiodiimide has been synthesised by the reaction of $(SN)_4$ with *N*-trimethylstannyldimethylamine[38] or with tris(trimethylstannyl)amine:[39]

$$(SN)_4 \left\langle \begin{array}{l} \xrightarrow{(Me_3Sn)_3N\ \text{or}\ Me_2SnNMe_2} (Me_3SnN{=})_2S\ ; \\ \xrightarrow{Me_2SiNAlk_2} Me_3Si{-}N{=}S{=}N{-}S{-}NAlk_2\,. \end{array}\right.$$

3. *N*-Alkyl-*N'*-arylthiodiimides

N-Sulphenylaniline combines with lithium *N*-alkyl-*N*-trimethylsilylamides in petroleum ether. Subsequent reaction of the adducts with aluminium chlorides leads to *N*-alkyl-*N'*-phenylthiodiimides:[40]

$$\begin{matrix} Alk \\ Me_3Si \end{matrix}\!\!>\!NLi \xrightarrow{Ph{-}NSO} \left[\begin{matrix} Alk \\ Me_3Si \end{matrix}\!\!>\!N{-}SO{-}N\!<\!\begin{matrix} Ph \\ Li \end{matrix}\right] \longrightarrow$$

$$\xrightarrow[-Al(OSiMe_3)_3]{AlCl_3} Ph{-}N{=}S{=}N{-}Alk\ ; \qquad Alk = Me,\ Et\,.$$

4. *NN'*-Diarylthiodiimides

The first diarylthiodiimides have been obtained by the condensation of *N*-sulphinylarylamines under the influence of metallic sodium.[41] *N*-Sulphinylaniline and its derivatives containing electron-donating substituents in the aromatic ring enter into this reaction. The yield of the products does not exceed 40%, which is probably associated with the elimination of sulphur from the thiodiimides on treatment with sodium to give azo-compounds. *N*-Sulphinylarylamines containing electron-accepting substituents do not undergo this reaction.[41]

N-Sulphinylarylamines also condense on treatment with alkali metal alkoxides, amides, and hydrides and dimsylsodium,[42–45] derivatives containing both electron-donating and electron-accepting groups in this ring undergoing the reaction. The most effective catalysts are alkali metal alkoxides and dimsylsodium. The yields of *NN'*-diarylthiodiimides are significantly higher than in the condensation of *N*-sulphinylamines under the influence of sodium.[42–45] The mechanism of the condensation of *N*-sulphinylarylamines on treatment with bases[43] is illustrated in Scheme (1) below

$$Ar{-}N{=}S{=}O \xrightarrow{B^-} \left[Ar{-}\overline{N}{-}S{=}O \;\big|\; B\right] \xrightarrow{Ar\text{-}NSO} \longrightarrow$$
$$\longrightarrow \left[\begin{matrix} Ar{-}N{-}S{=}O \\ \quad\quad\ \backslash B \\ \overline{O}{-}S{=}N{-}Ar \end{matrix}\right] \xrightarrow{-B^-} \qquad (1)$$
$$\rightarrow \left[\begin{matrix} Ar{-}N{=}S{-}O \\ \quad\quad\ | \\ Ar{-}N{-}S{=}O \end{matrix}\right] \xrightarrow{-SO_2} (Ar{-}N{=})_2S\,.$$

It has been reported that the condensation of *N*-sulphinylaniline to give diphenylthiodiimide proceeds on treatment with zerovalent nickel complexes; however, the yields are low (12–20%). Substituted *N*-sulphinylanilines (4-Me-, 4-EtCO-) do not react.[46]

The most general method of synthesis of symmetrical diarylthiodiimides involves the interaction of arylamines with sulphur tetrafluoride.[47–50] Compared with other procedures, this method gives higher yields of purer products. Arylamines containing both electron-donating and electron-accepting groups,[48] including polyfluoroarylamines,[49,50] enter into this reaction. An essential condition is the removal of the hydrogen fluoride evolved during the reaction. Trimethyl- and triethyl-amines[47,48] as well as sodium fluoride[49,50] have been used as HF acceptors. In the first stage of the reaction the corresponding *N*-aryl-*SS*-difluorosulphimine is formed from the amine and sulphur tetrafluoride and then gives rise to the thiodiimide by reacting with a second arylamine molecule:

$$R{-}NH_2 \xrightarrow[-HF]{SF_4} R{-}N{=}SF_2 \xrightarrow[-HF]{R{\cdot}NH_2} (R{-}N{=})_2S\ ;$$
$$R = Ar,\ Ar_f\ .$$

The last reaction leads to a convenient procedure for the synthesis of asymmetric *NN'*-diarylthiodiimides. Its synthetic possibilities have been demonstrated in relation to the interaction of arylamines with *N*-aryl-*SS*-dichlorosulphimines,[10,51] *SS*-dichloro-*N*-pentafluorophenylsulphimine,[52,53] and *SS*-difluoro-*N*-polyfluoroarylsulphimines.[50,52] The reactions proceed smoothly and with satisfactory yields. Triethylamine, pyridine, and sodium fluoride have been used to combine with HCl and HF.[10,50-52]

The interaction of SF_4 with *N*-aryliminotriphenylphosphoranes also leads to the diarylthiodiimides. The reaction proceeds via the intermediate formation of *N*-aryl-*SS*-difluorosulphimines, which also makes it possible to obtain asymmetric derivatives:[54]

$$Ph_3P{=}NAr \xrightarrow[-Ph_3PF_2]{SF_4} Ar{-}N{=}SF_2 \xrightarrow[-Ph_3PF_2]{Ph_3P{=}NAr'} Ar{-}N{=}S{=}N{-}Ar'\ .$$

On treatment with sulphur tetrachloride, aniline is chlorinated in the ring and a thiodiimide is not then formed.[47] However, on reaction with dichlorodisulphane in the presence of pyridine, certain aromatic amines react to form *NN'*-diarylthiodiimides, the yields of the pure products exceeding 70%:[55]

$$Ar{-}NH_2 \xrightarrow[-HCl;\ -S]{S_2Cl_2} (Ar{-}N{=})_2S\ ;$$
$$Ar = 4\text{-}C_6H_4{-}N{=}N{-}C_6H_5,\ 4\text{-}ClC_6H_4,$$
$$4\text{-}EtOCOC_6H_4,\ 1\text{-naphthyl}.$$

The reactions of pentafluoroaniline[56] and 2,4-di(t-butyl)-6-methylaniline[1] with dichloromonosulphane also lead to the corresponding thiodiimides. The second product of the reaction of 2,4-di(t-butyl)-6-methylaniline with SCl_2 is 2,4-di(t-butyl)-6-methyl-*N*thiosulphinylaniline.[1] It is noteworthy that, on reaction with a large excess of dichloromonosulphane, arylamines form *N*-aryl-*SS*-dichlorosulphimines.[57]

A convenient preparative version of the synthesis of *NN'*-diarylthiodiimides using S_2Cl_2 and SCl_2 as sources of sulphur involves the interaction of the latter with aryl-*NN*-bis(trimethylsilyl)amines. *N*-Thiosulphinylanilines and thionitrosoarenes are probably formed as intermediates in these processes.[58]

It has been shown in relation to the 2,4-di(t-butyl)-6-methyl derivative that the photolysis of *N*-thiosulphinylanilines leads to diarylthiodiimides.[59] The thermolysis of 2,4-di(t-butyl)-6-methyl-*N*-thiosulphinylaniline in boiling benzene leads to the formation of benzoisothiazole and an arylamine,[59] while the thermolysis of 2,4,6-tribromo-*N*-thiosulphinylaniline affords the corresponding thiodiimide.[24]

Diarylthiodiimides have also been synthesised under the conditions of the Pishchimuka reaction[60] and on interaction of *SS*-dichloro-*N*-pentafluorophenyl-sulphamine with hexamethyldisilathiane:[24]

$$Ar{-}NH_2 \xrightarrow[Hg(HNAc)_2]{S_8} (Ar{-}N{=})_2S\ ;$$
$$Ph_f{-}N{=}SCl_2 \xrightarrow[-Me_3SiCl]{S(SiMe_3)_2} [Ph_f{-}N{=}S{=}S] \xrightarrow[-S]{} (Ph_f{-}N{=})_2S\ .$$

Yet another method leading to the synthesis of diarylthiodiimides involves the transamination of *NN'*-di(arenesulphonyl)thiodiimides. In the reaction of arylamines with *NN'*-di(benzenesulphonyl)thiodiimide in molar proportions of 1:1, one sulphonyl-amino-group is replaced by an arylimino-group and *N*-aryl-*N'*-benzenesulphonylthiodiimides are formed. When the latter are treated with aniline or arylamines containing electron-donating substituents in the ring, either the arylimino- or benzenesulphonyl group is displaced. If the arylimino-group contains no electron-accepting substituents, the benzenesulphonylimino-group is displaced and *NN'*-diarylthiodiimide is produced. Aromatic amines containing electron-accepting groups in the ring do not react with *N*-aryl-*N'*-benzenesulphonylthiodiimides. The diamides of *N*-arenesulphonylamino- or *N*-arylimino-sulphurous acids are apparently formed as intermediates in the transamination reaction of *NN'*-di(arenesulphonyl)thiodiimides:[61]

$$(PhSO_2N{=})_2S \xrightarrow[-PhSO_2NH_2]{ArNH_2} Ar{-}N{=}S{=}N{-}SO_2{-}Ph \xrightarrow[-PhSO_2NH_2]{Ar'NH_2} Ar{-}N{=}S{=}N{-}Ar'\ .$$

5. *N*-Aryl-*N'*-arenesulphenylthiodiimides

N-Aryl-*N'*-arenesulphenylthiodiimides can be obtained by the reaction of the amides and imides of arenesulphenic acids with *N*-aryl-*SS*-dihalogenosulphimines and also with trithiazyl trichloride:[53]

$$Ph_f{-}S{-}NH_2 \xrightarrow[-HF]{Ph{-}N{=}SF_2} Ph_f{-}S{-}N{=}S{=}N{-}Ph\ ;$$
$$(PhS)_2NH \xrightarrow[-PhSCl;\ -HCl]{Ph_f{-}N{=}SCl_2} Ph{-}S{-}N{=}S{=}N{-}Ph_f\ ;$$
$$PhS{-}NH{-}Ph \xrightarrow[-HCl]{(NSCl)_3} Ph{-}S{-}N{=}S{=}N{-}Ph\ .$$

6. *N*-Aryl-*N'*-arenesulphonylthiodiimides

N-Aryl-*N'*-arenesulphonylthiodiimides can be obtained either by the transamination of bis(benzenesulphonyl)thiodiimides on treatment with an equimolar amount of an arylamine or by the reaction of *N*-arenesulphonyl-*SS*-dichlorosulphimines.[61,62] The only thiodiimide containing a heteryl substituent at the N=S=N group, namely *N*-benzenesulphonyl-*N'*-2-pyridylthiodiimide, has been obtained by the transamination of bis(benzenesulphonyl)thiodiimide with 2-aminopyridine and has been identified in the form of adducts with diene hydrocarbons.[63]

7. *NN'*-Di(arenesulphonyl)thiodiimides

When *NN*-dichloroamides of arenesulphonic acids are heated with sulphur in the absence of a solvent, chlorine is evolved and bis(arenesulphonyl)thiodiimides are produced in quantitative yields. It has been suggested that one of the intermediates in this reaction is the thio-analogue of a nitroso-compound, namely $Ar{-}SO_2{-}N{=}S$:[64]

$$Ar{-}SO_2{-}NCl_2 \xrightarrow[-Cl_2]{S} (Ar{-}SO_2{-}N{=})_2S \xleftarrow[-SO_2]{} O{=}S{=}N{-}SO_2{-}Ar\ .$$

However, heating of the *NN*-dichloroamides of pentafluorobenzene-sulphonic acid with sulphur affords the corresponding *SS*-dichlorosulphimine.[11]

The reactions of the *NN*-dichloroamides of arenesulphonic acids with sulphur chlorides and *N*-arenesulphonyl-*SS*-dichlorosulphimines, of arenesulphonamides[64] and hexamethyldisilathiane[24] with *N*-arenesulphonyl-*SS*-dichlorosulphonimines, and of *N*-arenesulphonyl-*SS*-bis(trimethylsilyl)sulphimines with dichloromonosulphane[24] also leads to bis(arenesulphonyl)-thiodiimides.

Another method of synthesis of bis(arenesulphonyl)thiodiimides involves the condensation of *N*-sulphinylarenesulphonamides. On treatment with $AlCl_3$ and tertiary amines, it occurs at 110–125 °C and at room temperature respectively, the yields of the bis(arenesulphonyl)thiodiimides being almost quantitative.[65]

Bis(benzenesulphonyl)thiodiimide has been obtained by heating *N*-sulphinylbenzenesulphonamide with *NN*-bis(trimethylsilyl)benzenesulphonamide:[66]

$$Ph{-}SO_2{-}NSO \xrightarrow[-(Me_3Si)_2O]{(Me_3Si)_2N{-}SO_2{-}Ph} (Ph{-}SO_2{-}N{=})_2S\ .$$

8. *N*-Arenesulphenyl-*N'*-arenesulphonylthiodiimides

N-Arenesulphenyl-*N'*-arenesulphonylthiodiimides are formed in low yields (5–7%) on reaction of trichloromethanesulphenyl chloride with the amides of arenesulphinic acids in boiling tetrachloroethylene. The main products of this reaction, whose mechanism is obscure, are diaryl disulphides and ammonium chloride:[67]

$$Ar{-}SO_2{-}NH_2 \xrightarrow[-(ArS)_2;\,-NH_4Cl]{Cl_3C{-}SCl} Ar{-}SO_2{-}N{=}S{=}N{-}S{-}Ar\ ;$$
$$Ar = Ph,\ Tol,\ 4\text{-}Cl{-}Ph\ .$$

N-Arenesulphinyl-*N'*-arenesulphonylthiodiimides have also been synthesised by the transamination of *NN'*-bis(arenesulphonyl)thiodiimides. For example, a mixed *N*-sulphenyl-*N'*-sulphonylthiodiimide is formed in satisfactory yield in boiling benzene from 2-nitrobenzenesulphenamide and ditosylthiodiimide; the reaction is catalysed by pyridine. In the presence of pyridine, the transamination of ditosylthiodiimide is also observed on treatment with *N*-sulphinylarenesulphenamides, but the yields are in this case only 10–17%. *N*-2-Nitrobenzenesulphenyl-*N'*-tosylthiodiimide has been synthesised from *SS*-dichloro-*N*-tosylsulphinamine and 2-nitrobenzenesulphenamide:[68]

$$(TosN{=})_2S \xrightarrow[-TosNX]{ArSNX} Tos{-}N{=}S{=}N{-}S{-}Ar \xleftarrow[-HCl]{ArSNH_2} TosN{=}SCl_2\ ;$$
$$X = H_2,\ SO;\ Ar = 2\text{-}O_2N{-}Ph\ .$$

9. *NN'*-Bis(arenesulphenyl)thiodiimides

The most general method of synthesis of bis(arenesulphenyl)thiodiimides involves the interaction of bis(trimethylsilyl)thiodiimide with arenesulphenyl chlorides.[2] This method makes it possible to obtain also asymmetric *NN'*-bis-(arenesulphenyl)thiodiimides by a two-stage reaction. In the reaction of bis(trimethylsilyl)thiodiimide with arenesulphenyl chloride in molar proportions of 1:1, the first stage involves the formation of *N*-arenesulphenyl-*N'*-trimethylsilylthiodiimide, which can be made to react with a secondary arenesulphenyl chloride molecule.[2]

$$(Me_3Si{-}N{=})_2S \xrightarrow[-Me_3SiCl]{ArSCl} Ar{-}S{-}N{=}S{=}N{-}SiMe_3 \xrightarrow[-Me_3SiCl]{Ar'SCl} \rightarrow Ar{-}S{-}N{=}S{=}N{-}S{-}Ar'.$$

Compounds containing a five-membered sulphur–nitrogen chain are also formed when sulphur nitride $(SN)_4$ reacts with diazo-compounds[7,69] and arylmagnesium bromides[70–72] but in the latter case the main products are diaryl disulphides:[71]

$$(SN)_4 \begin{cases} \xrightarrow{ArMgBr} [(SN)_4\cdot 2ArMgBr] \xrightarrow{H_3O^+} (Ar{-}S{-}N{=})_2S; \\ \xrightarrow[-N_2]{R_2CN_2} (R_2C{=}N{-}{-}N{=})_2S + R_2C\!\!<\!\!\begin{matrix}S\\ \diagup\diagdown\\ CR_2\end{matrix} \end{cases}.$$

Apart from the reactions listed above, several other processes leading to bis(arenesulphenyl)thiodiimides are known. Thus, when *N*-2-nitrobenzenesulphenyl-*N'*-tosylthiodiimide is refluxed in a mixture of benzene and morpholine (catalyst), it is symmetrised to form bis(2-nitrobenzenesulphenyl)thiodiimide. The same product has been obtained from *N*-2-nitrobenzenesulphenyl-*SS*-dichlorosulphimine and 3-nitroaniline and from 2-nitrobenzenesulphenamide and dichloromonosulphane.[68]

N-Benzenesulphenyl-*N'*-pentafluorobenzenesulphenylthiodiimide[53] and bis(pentafluorobenzenesulphenyl)thiodiimide[73] have been obtained by treating *N*-benzenesulphenyl-*N'*-pentafluorobenzenesulphenylamine and *NN*-bis(pentafluorobenzenesulphenyl)amine respectively with trithiazyl trichloride. Bis(pentafluorobenzenesulphenylthiodiimide) has also been obtained from SF_4 and pentafluorobenzenesulphenamide.[74] Bis(benzenesulphenyl)thiodiimide has been synthesised from thiodithiazyl dichloride $S_3N_2Cl_2$ and phenylmagnesium bromide.[72] The reaction of the tetrathiotetraimide $(SNH)_4$ with the corresponding arenesulphonyl chloride yielded bis(2,5-dichlorobenzenesulphenyl)- and bis(2,5-6-trichlorobenzenesulphenyl)-thiodiimides:[75]

$$(NSCl)_3 \xrightarrow[HCl]{RS{-}NH{-}SPh_f} R{-}S{-}N{=}S{=}N{-}S{-}Ph_f\ ;$$
$$R = Ph,\ Ph_f$$
$$(SNH)_4 \xrightarrow[-HCl;\,-SO_2]{ArSO_2Cl} (Ar{-}S{-}N{=})_2S\ .$$

10. *N*-Aryl-*N'*-phosphorylthiodiimides

Thiodiimides containing the phosphoryl group are formed when the *NN*-dichloroamides of dialkylphosphoric acids react with *SS*-dichlorosulphimines or hexamethyldisilathiane. It has been suggested that one of the intermediates in the latter reaction consists of thionitroso-compounds.[76] *N*-Phenyl-*N'*-(phenylphosphoramidyl)thiodimide has been obtained by the reaction of aniline with *SS*-dichloro-N-dichlorphosphoryl-sulphimine:[62]

$$(AlkO)_2P(O)NCl_2 \begin{cases} \xrightarrow[-Cl_2]{Cl_2S{=}NR} (AlkO)_2P(O)N{=}S{=}NR\ ; \\ \xrightarrow[-Me_3SiCl]{S(SiMe_3)_2} [(AlkO)_2P(O)N{=}]_2S\ ; \end{cases}$$
$$R = Alk,\ SO_2Ar,\ P(O)(Alk)_2\ ;$$
$$Cl_2P(O)N{=}SCl_2 \xrightarrow[-HCl]{PhNH_2} Ph{-}N{=}S{=}N{-}P(O)(HNPh)_2.$$

11. *NN'*-Diaroylthiodiimides

Diaroylthiodiimides are produced (a) by the condensation of *N*-sulphinylbenzamides or by the reaction of benzamides with thionyl chloride, (b) by the reaction of *N*-chlorobenzamide with sulphur, and (c) by the reaction of *NN'*-diaroylamides of sulphoxylic acid with the *NN*-dichloroamides of sulphonic acids. All the reactions take place in the presence of pyridine. Dibenzoylthiodiimide has also been obtained by the reduction of methyl *N*-chloroiminobenzoate with sulphur or *N*-benzoyl-*SS*-dichlorosulphimine:[77,78]

$$\left.\begin{array}{l} ArCONH_2 \xrightarrow{SOCl_2} ArCO{-}NSO \xrightarrow{-SO_2} \\ ArCONHCl \xrightarrow{S} \\ (ArCONH_2)S \xrightarrow[-Ar'SO_2NH_2;\,-HCl]{Ar'SO_2NCl_2} \end{array}\right\} \longrightarrow (ArCO{-}N{=})_2S;$$
$$PhC(OMe){=}NCl \xrightarrow[-MeCl]{S \text{ or } -MeCl,\,-Cl_2}{Cl_2S{=}N{-}COPh} (PhCO{-}N{=})_2S\ .$$

One of the mechanisms proposed for the interaction of *N*-chlorobenzamides with sulphur[77] involves the dehydrochlorination of *N*-chlorobenzamide with pyridine and the subsequent interaction of aroylnitrene with sulphur. The second mechanism proposed is illustrated schematically below:

$$ArCONCl \xrightarrow{S} ArCO{-}NH{-}SCl \xrightarrow[-Cl_2]{ArCONHCl} \rightarrow (ArCONH)_2S \xrightarrow[-HCl]{Cl_2} (ArCO{-}N{=})_2S\ .$$

The interaction of the *NN*-dichloroamide of pentafluorobenzoic acid with sulphur leads to *SS*-dichloro-*N*-pentafluorobenzoylsulphimine.[11]

12. *NN'*-Bis(alkoxycarbonyl)thiodiimides

Bis(alkoxycarbonyl)thiodiimides have been synthesised from *NN*-dichlorourethanes on treatment with sulphur, dichloromonosulphane, or *N*-alkoxycarbonyl-*SS*-dichlorosulphimines. The reactions take place readily on heating the starting materials in the absence of a solvent and are accompanied by the evolution of chlorine:[79]

$$AlkO{-}CO{-}NCl_2 \xrightarrow[-Cl_2]{S,\ or\ SCl_2,\ or\ Cl_2S{=}N{-}COOAlk} (AlkOCO{-}N{=})_2S\ ;$$
Alk = Me, Et .

13. *N*-Alkyl(acyl)-*N'*-bromothiodiimides

N-Alkyl(acyl)-*SS*-dichlorosulphimines react with *N*-bromohexamethyldisilazane to form *N*-alkyl(acyl)-*N'*-bromothiodiimides:[80]

$$(Me_3Si)_2NBr \xrightarrow[-Me_3SiCl]{R{-}N{=}SCl_2} R{-}N{=}S{=}N{-}Br\ ;$$
$R = Alk_2C(CN),\ ArCO{-},\ ArSO_2{-}$

14. Compounds Containing More than One N=S=N Group in the Sulphur–Nitrogen Chain

When bis(trimethylsilyl)thiodiimide reacts with dichloromonosulphane in molar proportions of 2:1, 1,7,bis(trimethylsilyl)trithiotetranitride is formed, its sulphur–nitrogen chain consisting of two thiodiimide groups linked by a sulphide bridge.[81] The same substance has been obtained by the reaction of trithiazyl trichloride with hexamethyldisilazane.[31,82] 1,7-Bis(pentafluorophenyl) and 1,7-di-t-butyl-trithiotetranitrides have been synthesised from pentafluoro-*NN*-bis(trimethylstannyl)aniline and $S_3N_2Cl_2$ [83] or from *N*-t-butyl-*N'*-trimethylsilylthiodiimide and dichloromonosulphane[33,84] respectively:

$$\left.\begin{matrix}(Me_3Si{-}N{=})_2S \xrightarrow[-Me_3SiCl]{SCl_2} \\ (Me_3Si)_2NH \xrightarrow[-HCl]{(NSCl)_3}\end{matrix}\right\} \rightarrow (Me_3Si{-}N{=}S{=}N{-})_2S\ ;$$

$$Ph_f{-}N(SnMe_3)_2 \xrightarrow{S_3N_2Cl_2} (Ph_f{-}N{=}S{=}N{-})_2S\ ;$$

$$Me_3Si{-}N{=}S{=}N{-}Bu\text{-}t \xrightarrow[-Me_3SiCl]{SCl_2} (t\text{-}Bu{-}N{=}S{=}N{-})_2S$$

1,9-Diarylpentathiotetranitrides,[2] compounds which are known at present to have the longest (for non-polymeric molecules) sulphur–nitrogen chains, are obtained by the reaction of *N*-2-nitrobenzenesulphenyl- and *N*-2,4-dinitrobenzenesulphenyl-*N'*-trimethylsilylthiodiimides with dichloromonosulphane:

$$Ar{-}S{-}N{=}S{=}N{-}SiMe_3 \xrightarrow[-Me_3SiCl]{SCl_2} (Ar{-}S{-}N{=}S{=}N{-})_2S\ .$$

When an attempt was made to obtain an even longer sulphur–nitrogen chain by the reaction of dichloromonosulphane with 1,7-bis(trimethylsilyl)trithiotetranitride, only sulphur nitride $(SN)_4$ was obtained.[81]

15. Poly(arylenethiodiimides)

The condensation of aromatic *NN'*-disulphinyldiamines catalysed by potassium or lithium t-butoxides leads to poly(arylenethiodiimides). Polymers with *p*-phenylene units in the chain are almost insoluble in organic solvent. The derivatives containing *m*-aniline units are soluble in some cases; they are apparently macrocyclic. The determination of the molecular weight of a soluble polymer obtained from bis(3-*N*-sulphinylamino-4-methoxyphenyl)methane yielded a value corresponding to the octamer.[5,6]

Poly(arylenethionitrides) have been obtained from sulphur nitride $(SN)_4$ and phenylenebisdiazoalkanes.[85] The determination of the molecular weight of one of them (R = Ph, Ar = C_6H_4) showed that it is a trimer:

$$RC{-}Ar{-}CR \xrightarrow[-N_2]{(SN)_4} \rightarrow (-Ar{-}C{=}N{-}S{-}N{=}S{=}N{-}S{-}N{=}C{-}Ar{-}\underset{\displaystyle S}{\overset{\displaystyle C}{\diagup\diagdown}}{-})_n\ .$$

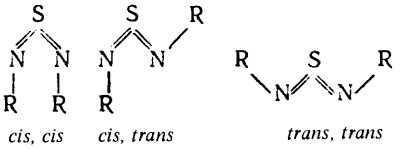
III. GEOMETRY AND ELECTRONIC STRUCTURE

Dialkyl-, diaryl-, and bis(arenesulphonyl)-thiodiimides exist predominantly in the form of *cis,trans*-isomers with a small admixture (in solution) of *trans,trans*-isomers. When a longer sulphur-nitrogen chain is incorporated in the composition of the compound, the thiodiimide group is retained as an independent structural unit, but the molecules of bis(arenesulphenyl)thiodiimides now have the *cis,cis*-geometry. Five-membered sulphur–nitrogen chains in organic derivatives are just as planar as the "infinite" $(SN)_x$ macromolecules.

The electronic structure of the thiodiimide group in organic derivatives is extremely sensitive to the influence of substituents and is capable of undergoing a significant rearrangement under their influence. In aromatic derivatives the thiodiimide group conjugated with organic fragments is a weak electron donor and transmits the electronic effects of substituents. At the same time many important details of the electronic structure of the organic thiodiimides remain obscure and require further study.

1. The Geometry of the Molecules of Organic Thiodiimides

Theoretically, organic thiodiimides can exist in the form of three geometrical isomers:



cis, cis *cis, trans* *trans, trans*

According to electron diffraction[86] and X-ray diffraction[86,87] data, the molecules of dimethylthiodiimides in the gas phase and of di-*p*-tolyl- and ditosyl-thiodiimides in the crystalline form have the *cis,trans*-configuration, the bond lengths and valence angles of which are given in Table 1. The lengths of the SN bonds in the thiodiimides are significantly closer to

the value for the sulphur–nitrogen double bond (1.52 Å) than for the single bond (1.74 Å). The distance between the nitrogen atoms rules out a valence interaction between them.[87]

Table 1. Parameters of the molecules of certain organic thiodiimides R–N=S=N–R.*

R	Bond lengths, Å				Valence angles, deg		
	SN_{cis}	SN_{trans}	NR_{cis}	NR_{trans}	RNS_{cis}	RNS_{trans}	NSN
Tol	1.53	1.56	1.46	1.41	131	118	117
Tos	1.52	1.52	1.68	1.69	125	117	115
Me	1.53	1.53	1.46	1.46	125	117	114

*According to the data of Kuyper et al.[86] and Leandri et al.[87]

The carbon, nitrogen, and sulphur atoms in the molecule of dimethylthiodiimide lie in the same place.[86] However, analysis of the vibrational spectra of bis(trimethylsilyl)thiodiimide led Herbrechtshmeier et al.[88] to the conclusion that the planar conformation of the $(SiN=)_2S$ fragment with C_{2v} or C_s point symmetry is ruled out and that a non-planar conformation with C_2 point symmetry is most probable.[88]

There is a deviation from planarity also in the molecule of di-*p*-tolyl-thiodiimide: in the crystalline state the planes of the aromatic rings form dihedral angles of 21.9° and 39.9° with the plane of the NSN atoms;[87] it may be that this is associated in the first place with the characteristic features of the crystal packing.

In solution dialkyl-[22,89] and diaryl-thiodiimides[48] exist in the form of an equilibrium mixture of the *cis,trans*- and *trans,trans*-isomers according to ^{13}C and ^1H NMR, the former isomer being always present in a greater amount. In the case of the dimesitylthiodiimide, only the *trans,trans*-isomer is present for steric reasons.[48] The activation energy for the interconversion of the isomers of diarylthiodiimide is in the range 11–12 kcal mol^{-1} and the frequency factor is approximately 10^{13} s^{-1}, which is usual for unimolecular reactions with an unstrained transition state. The electron-donating groups in the 4,4'-positions in the aromatic rings diminish the rate of interconversion of the isomer. The rates of the interconversions of the isomers of dialkylthiodiimides are lower than those for the diaryl derivatives.[22,48]

The increase in the length of the sulphur–nitrogen chain on passing from diaryl- to bis(arenesulphenyl)-thiodiimides is accompanied by changes in molecular geometry. According to X-ray diffraction data, the arenesulphenyl fragments in the molecules of bis(benzenesulphenyl)thiodiimide[90] and bis-(4-chlorobenzenesulphenyl)thiodiimide[91] are located in the *cis,cis*-positions relative to the central N=S=N unit. The distances between the nitrogen atoms and the central sulphur atom typical for SN double bonds agree well with the values found for di-*p*-tolylthiodiimide (Table 1). The distances between the nitrogen atoms and the sulphur atoms at the edges (1.66 Å) have the usual values for SN single bonds, in which there is the possibility of some d_π–p_π overlap.[91] The distance between the extreme sulphur atoms (3.29 Å) greatly exceeds the length of the covalent SS bond, but is somewhat smaller than the sum of the van der Waals radii of two sulphur atoms, which may indicate a weak interaction. The valence angle at the central sulphur atom is 124° and those at the nitrogen atoms are 129° and 126°.[91]

The most characteristic features of the steric structure of the bis(4-chlorobenzenesulphenyl)thiodiimide molecule is its close approximation to planarity (a single plane with an average deviation of the atoms of 0.11 Å and a maximum deviation of 0.24 Å can be adopted for the entire molecule) and the virtual collinearity of the axes of the aromatic rings (the projections of the lines passing through the Cl and S atoms in each of the 4-chlorobenzenesulphenyl groups onto the plane of the molecule form an angle of 190°).[91] However, the benzene rings in the bis(benzenesulphenyl)thiodiimide molecule have been rotated by 30.8° relative to the average plane of the nitrogen and sulphur atoms.[90]

The latest of the open-chain thiodiimides whose real geometry is known is 1,5-bis(diphenylmethyleneimino)trithiodinitride $Ph_2C=N-S-N=S=N-S-N=CPh_2$. The central sulphur atom of the molecule is located on a twofold symmetry axis; the valence angle at this atom is 124°. The substituents are located in the *cis,cis*-positions relative to the central N=S=N unit. The five central atoms of the sulphur–nitrogen chain are located in the same plane (with deviations within the limits of 0.04 Å), while the remaining two nitrogen atoms deviate from this plane by 0.49 Å. The SN bond lengths in the =S=N–S–N= fragment are respectively 1.55, 1.66, and 1.69 Å; the valence angles at the nitrogen atoms of the central N=S=N unit are 126°.[92,93]

It is of interest to compare the geometry of the molecules of organic thiodiimides with the geometry of the macromolecules of the polymeric sulphur nitride $(SN)_x$, which consist of chains of alternating sulphur and nitrogen atoms.[3,4] If one isolates an arbitrary NSN fragment in the $(SN)_x$ macromolecule, then the chain is continued in the *cis,trans*-positions, in a manner resembling the disposition of the substituents in the *cis,trans*-positions relative to the thiodiimide group in dialkyl, diaryl, and bis(arenesulphonyl) derivatives. However, the SN bond lengths in $(SN)_x$, which alternate (1.63 and 1.59 Å), appreciably exceed those in the thiodiimide group. The valence angles at the sulphur atoms in the $(SN)_x$ molecule are 106°, which is much less than the angle at the sulphur atom of the thiodiimide group. The valence angles at the nitrogen atoms (120°) are somewhat greater than the angles at the nitrogen atom of the N=S=N group linked to a *trans*-substituent, but are smaller than at the nitrogen atom linked to a *cis*-substituent.

2. The Electronic Structure of the Molecules of Organic Thiodiimides

(a) Electronic spectroscopic data and the results of quantum-chemical calculations. According to the data of Schouten and Oskam[94] and Kroner et al.,[95] the He(I) photoelectron spectra of dialkylthiodiimides contain three distinct peaks separated from a series of poorly resolved bands (with the exception of the spectrum of the diethyl derivative in which five peaks are resolved[94]). The interpretation of the spectra in terms of the Koopmans theorem on the basis of the quantum-chemical calculation by the LCAO-MO SCO method in terms of the CNDO/2 valence approximation, including the 3*d* AO of sulphur in the basis set, showed[94] that the first ionisation potential (IP) corresponds to the removal of an electron from the π MO made up of the d_{yz} AO of sulphur and the p_z AO of nitrogen. The next two bands correspond to the ionisation of orbitals of the σ type, the first of which constitutes a symmetrical combination of the AO ("unshared pairs") of nitrogen and sulphur and the second an antisymmetric combination of the AO ("unshared pairs") of nitrogen without the participation of the AO of sulphur. The fourth

band (usually a shoulder against the background of the ionisation of the σ skeleton) corresponds to the ionisation of the π MO made up of the p_z AO of nitrogen and sulphur. Comparison of the results of calculations by the CNDO/2 method for the *cis,trans*- and *trans,trans*-isomers of dimethylthiodiimides shows certain differences between the one-electron MO energies while their sequence is the same.[94] The MO in Table 2, which summarises the photoelectron spectroscopic data for dialkylthiodiimides, are therefore classified in terms of the irreducible representations of the symmetry point group C_{2v} of *trans,trans*-dimethylthiodiimide.

Table 2. The vertical ionisation potentials (IP) and one-electron MO energies of dialkylthiodiimides $(AlkN=)_2S$.*

IP, eV				One-electron MO energies**, eV (Alk = Me)		Assignment*
Me	Et	iso-Pr	t-Bu	*cis, trans*	*trans, trans*	
9.16	8.90	8.75	8.61 (8,65)	12.37	12.25	a_2 (a_2)
9.86	9.62	9.43	9.06 (9,01)	13.37	13.03	a_1 (a_1)
10.55	10.26	10.05	9.57 (9,60)	13.58	14.15	b_1 (b_2)
11.91	11.62	11.34	11.10 (11,1)	14.81	14.90	b_2 (b_1)
12.85	12.2	11.7	11.6	16.45	16.84	b_1

*According to the data of Schouten and Oskam[94] (the data of Kroner et al.[95] are given in brackets).
**Quoted with the sign reversed.

The substitution of the alkyl groups by trimethylsilyl groups alters the sequence of the MO. Interpretation of the He(I) photoelectron spectrum of bis(trimethylsilyl)-thiodiimide on the basis of the quantum-chemical calculations in terms of the MINDO approximation using the Koopmans theorem showed that the first three vertical IP (IP_1 = 9.2 EV) correspond to the MO with a predominant contribution by the AO of nitrogen: the non-bonding $a_2(\pi)$ MO made up of the p_z AO of nitrogen and the antisymmetric (b_2) and symmetrical (a_1) combinations of the AO of the "unshared pairs" of nitrogen.[96]

However, one should note that the interpretation of the photoelectron spectra on the basis of theoretical calculations alone, which are usually semiempirical, is not reliable and must be treated with caution. Calculations in terms of the CNDO approximation frequently yield an incorrect sequence of the orbitals, in particular certain σ MO are placed above the π MO.[97]

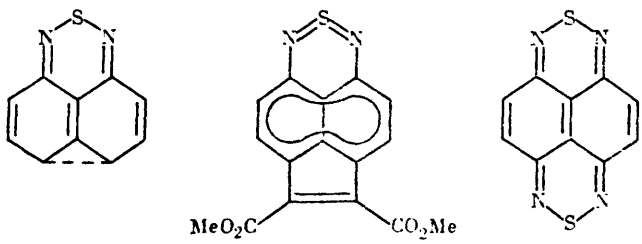
An increase in the length of the sulphur–nitrogen chain entails a decrease of the first IP. Thus IP_1 = 7.85 eV for 1,7-bis(trimethylsilyl)trithiotetranitride.[96]

Organic thiodiimides containing aromatic substituents have not been investigated by photoelectron spectroscopy with the exception of naphtho[1,8-*cd*]-1,2,6-thiadiazine, whose He(I) spectrum proved to be similar to that of 2-methyl-naphtho-[1,8,*de*]-1,2,6-triazine. A great similarity has also been observed between the electronic absorption spectra. The interpretation of the spectra based on calculations by the extended Hückel method and in terms of the MINDO/3 approximation has been carried out on the assumption that the bands in the electronic absorption spectra are associated with $\pi \rightarrow \pi^*$ transitions and that the Koopmans theorem holds for the photoelectron spectra; this interpretation showed the observed similarity between the spectra is due to the similarity between the structures of the valence levels. Thus it follows that, in considering the thiodiimide group, one can neglect the structure with quadrivalent sulphur (−N=S=N−) and the group can be described in terms of the superposition of structures of type (2). In terms of the LCAO-MO theory, this means that the 3*d* AO of sulphur are unimportant for the ground and excited states of the thiodiimide group:[98]

$$R-\bar{N}-\overset{+}{S}=N-R \longleftrightarrow R-N=\overset{+}{S}-\bar{N}-R \,. \qquad (2)$$

However, one can adduce certain considerations in support of the view that the conclusions valid for a system such as naphtho[1,8-*cd*]-1,2,6-thiadiazine can be hardly extended to derivatives of an organic compound with the thiodiimide group, at any rate without special stipulations.

In the first place, one should note that the 3*d* AO of sulphur, which appear in semiempirical quantum-chemical calculations, are usually no more than correction functions applied to an incorrect basis set, which are of purely methodological importance,[99] and the results of such calculations cannot serve as reliable arguments in the solution of the problem of the involvement or non-involvement of the 3*d* AO of sulphur in the formation of a chemical bond. The 3*d* AO of sulphur are capable of participating effectively in the formation of a chemical bond only when there is a large positive charge on the sulphur atom. The population of the 3*d* AO is usually small and their role consists of not so much in increasing the strength of the bonds as in converting the non-bonding MO into bonding MO and in decreasing the anti-bonding character of the antibonding MO.[100] The charge on the sulphur atom of naphtho[1,8,-*cd*]-1,2,6-thiadiazine is unknown, but in certain thiodiimides (see below) it is sufficiently high to permit the involvement of the 3*d* AO of sulphur in bonding. Furthermore, naphtho[1,8-*cd*]-1,2,6-thiadiazine has a number of features which distinguish it from open-chain thiodiimides. In particular, one can consider the quinonoid structures (A) for this compound with a formal π-bond between the carbon atoms in the 4- and 5-positions, which agrees with the fact that it reacts with bis-(methoxycarbonyl)acetylene to form the acenaphthothiadiazine (B) via [12π + 2π]-cycloaddition and aromatisation.[101] The position of the ^{15}N NMR signal of naphtho[1,8-*cd*]1,2,6-thiadiazine in a weaker field compared with that of diphenyl-thiodiimide can be accounted for[102] by the contribution of this structure. Naphtho[1,8-*cd* : 4,5-*c'd'*]bis-1,2,6-thiadiazine, which is a very close analogue of naphtho[1,8-*cd*]-1,2,6-thiadiazine, is a weakly aromatic compound and its structure (C) probably contributes to its ground state.[103]



(A) (B) (C)

Organic compounds containing the thiodiimide group have not been investigated systematically by X-ray electronic spectroscopy. The determination of the bond energies E_b of the internal levels of the nitrogen and sulphur atoms in di-t-butylthiodiimide [$E_b(S_{2p_{3/2}})$ = 166.9 eV; $E_b(N_{1s})$ = 398.4 eV][95] and bis(trimethylsilyl)thiodiimide [$E_b(S_{2p})$ = 164.9 eV; $E_b(N_{1s})$ = 397.5 eV][81] showed that the E_b for the N_{1s} level and hence the effective charge on the nitrogen atom can change significantly as a function of the substituents to

which the N=S=N group is linked.# This agrees with the results of measurements of the effective charges on the sulphur atoms in organic thiodiimides by X-ray fluorescence spectroscopy. The positive charges within the volume defined by the covalent radius, determined from the shifts of the S K_α lines, vary within the following ranges (in units of the electronic charge): 0.28–0.33 for diarylthiodiimides, 0.24–0.36 for *N*-aryl-*N'*-polyfluoroarylthiodiimides, and 0.25–0.35 for bis(polyfluoroaryl)thiodiimides.[50] The charge on the sulphur atom in these compounds exceeds that in bis(pentafluorophenyl)disulphide, the X-ray spectroscopic study of which (S $L_{II,III}$ spectrum) showed that the 3*d* AO of sulphur are not involved in the formation of the chemical bond in this compound.[105] Thus the charges on the sulphur atom in the thiodiimide group linked to aryl and (or) polyfluoroaryl substituents do not rule out the possibility of the involvement of the 3*d* AO of sulphur in chemical bonding.

The distribution of the 3*p* electrons of the sulphur atoms among the MO in diarylthiodiimides and *N*-aryl-*N'*-polyfluoroarylthiodiimides (according to S K_β spectra) resembles that in aromatic sulphides. On passing to bis(polyfluoroaryl)thiodiimides, the character of the distribution of the 3*p* electrons of sulphur among the MO changes sharply and becomes similar to the distribution of the 3*p* electrons of sulphur among the MO in SO_2.[50] This result has been interpreted[50] as a consequence of the significant weakening of the effectiveness of the p_π–p_π interaction between the heteroatom and the polyfluoroaryl group linked to it compared with the aryl group;[106] this shows that the electronic structure of the thiodiimide group is extremely sensitive to the influences of the substituents and can undergo an appreciable rearrangement under such influence. An alternative explanation consists in a possible increase of symmetry from C_s to C_{2v} on passing from diaryl- to bis(polyfluoroaryl)-thiodiimides (i.e. on passing from the *cis,trans*-configuration to the *trans,trans*-configuration), but direct structural information does not exist.

The agreement between the effective charges on the sulphur atoms in the molecules of bis(4-methyl-2,3,5,6-tetrafluorophenyl)thiodiimides[50] and the polymeric sulphur nitride $(SN)_x$ [107] molecules makes it possible to compare[108] the S K_β spectra of these compounds directly in terms of the scale of the transition energies. The comparison shows that, in the short-wavelength region (~2468–2473 eV), where transitions from the π^* antibonding and π bonding MO are manifested in the S K_β spectrum of the sulphur nitride $(SN)_x$,[107] the spectra are similar as regards the form of the spectral line and the energies of its structural elements. From this it follows that populated π^* MO, antibonding in sulphur–nitrogen bonds, exist in bis(polyfluoroaryl)thiodiimides.

Calculations of the MO of dimethylthiodiimide in terms of the CNDO/2 approximation taking into account the 3*d* AO of sulphur showed[94] that the π^* antibonding MO in this molecule is unoccupied, being only virtual (LUMO). The antibonding π^* MO in the ground state can be populated only as a result of the interaction of the group π orbitals of the NSN fragment with the group π orbitals of the aromatic rings. The existence of the π interaction of the NSN group with aromatic substituents is also indicated by the changes in the relative intensities and width of the bands in the S K_β spectra of thiodiimides with aromatic (including polyfluorinated) substituents when the groups in the 4,4'-positions in the rings are varied.[50] This interaction leads to the existence of a series of many-centre MO, embracing both the NSN fragment and the aromatic rings, i.e. to the delocalisation of the π bonding throughout the molecule, which is outwardly expressed by the ability of the thiodiimide group to transmit the electronic influences of the substituents. A study of the ^{19}F NMR spectra of the compounds C_6F_5–N=S=N–C_6H_4–X-4 showed[50] that the relative chemical shift (relative to X = H) of the signal of the *p*-fluorine atom in the pentafluorophenyl ring is satisfactorily correlated with the Hammett σ_p constant of the substituent X.

In the electronic spectra of the organic thiodiimides R–N=S=N–R the long-wavelength absorption maximum undergoes a bathochromic shift on passing from alkyl or acyl derivatives (R = alkyl, AlkOCO, or $ArSO_2$) to monoaryl and further to diaryl derivatives.[51] In a series of symmetrical diarylthiodiimides both electron donating and electron accepting substituents in the 4,4'-positions in the rings induce a bathochromic shift of the long-wavelength absorption maximum[51] (Table 3). The characteristic long-wavelength absorption bands of symmetrical diarylthiodiimides are almost insensitive to the influence of solvents, while symmetrical derivatives of the type 4-$O_2NC_6H_4N$=S=NC_6H_4X-4 and $C_6H_5SO_2N$=S=NC_6H_4X-4 exhibit negative solvatochromism.[51] The long-wavelength absorption band in the electronic spectra of compounds of the latter two types is extremely sensitive also to the character of the substituents in the aromatic rings.[109] Electron-donating substituents X shift the absorption maximum towards longer wavelengths and the magnitude of the shift of λ_{max} (relative to the λ_{max} of the analogous compound with X=H) is satisfactorily correlated with the Hammett or Taft constant for the majority of substituents X. Electron-accepting substituents X hardly influence the position of the maximum or shift it towards shorter wavelengths. On the basis of the facts described, it has been concluded[109] that the band considered is apparently associated with the electron transfer not through the entire π system of the molecule but mainly through the unoccupied 3*d* AO of the sulphur.

Table 3. The long-wavelength absorption maxima in the electronic spectra of certain organic thiodiimide R–N=S=N–R.

R	λ_{max}, nm (lg ϵ)	Solvent	Refs.
t-Bu	276	*	[92]
Me_3Si	273 (~4)	Chloroform	[2]
Me_3Si	271.5	*	[92]
Ph	410 (3.98)	Ethanol	[47]
Ph	418	Ethanol	[51]
Ph	420 (4.07)	Benzene	[51]
4-$O_2NC_6H_4$	431 (4.26)	Benzene	[51]
4-$Me_2NC_6H_4$	532 (4.50)	Benzene	[51]
C_6F_5	390	Hexane	[49]
PhS	452	Dioxan	[85]
PhS	446	Acetonitrile	[72]
Ph_2C=NS	508	Benzene	[69]

*In the gas phase.

An increase in the length of the sulphur–nitrogen chain is accompanied by a bathochromic shift of the long-wavelength of the absorption maximum, which has been interpreted[2] as a consequence of the increase of the electron delocalisation along the chain. λ_{max} of the long-wavelength band varies

#Provided that this result is not associated with an error in calibration. The spectrum has been calibrated[95] in accordance with the exact value $E_b(C_{1s})$ = 285.0 eV;[104] Lidy et al[81] could not deal with this question in detail. According to Lindberg and Hedman,[104] the absolute values of E_b quoted in the early studies, based on a calibration in terms of the C_{1s} line, must be increased by 1 eV. If this applies to the study of Lidy et al,[81] then the E_b for the N_{1s} level in the compounds under discussion are virtually identical.

in the range 382–413 nm for the compounds $ArSN{=}S{=}NSiMe_3$, 448–476 nm for $(ArSN{=})_2S$, and 580–587 nm for $(ArSN{=}S{=}N)_2S$. Since electron-accepting substituents in aryl rings increase slightly the bathochromic shift, the delocalisation of the π bonding apparently embraces also the aromatic rings.[2]

Theoretical interpretation of the electronic absorption spectrum of diphenylthiodiimide on the basis of the p_π model of sulphur shows that the properties of this and similar compounds described here are associated with the presence of the quasi-polymethine chromophore NSN and the idea that the 3*d* AO of sulphur are involved is not essential for their understanding.[110] The long-wavelength absorption band is associated with the $\pi \rightarrow \pi^*$ transitions. The first excited state of diphenylthiodiimide can be described, in terms of the "molecules in the molecule" method, by a superposition of the locally excited (LE) configuration of the thiodiimide group and the configuration with charge transfer (CT) from the N=S=N fragment to the phenyl group. Comparison of the calculated spectroscopic characteristics of diphenylthiodiimide and the hypothetical *N*-hydro-*N'*-phenylthiodiimides indicates the importance of the presence of two phenyl substituents in the molecule of the former compound. The study of the interaction between the LE configuration of the N=S=N group and the N=S=N–phenyl CT configuration showed that the energy level of the first excited state is split by the CT configuration with participation of the second benzene ring.[110]

The energies of the $\pi \rightarrow \pi^*$ transitions in dimethylthiodiimides, benzo-2,1,3-thiadiazole, and naphtho[1,8-*cd*]-1,2,6-thiadiazine, evaluated from the results of the calculation by the CNDO/2 method using the virtual orbital approximations for the excited states, agree directly with experiments. The inclusion of the 3*d* AO of sulphur in the basis set lowers the HOMO energy, which increases the energy of the electronic transition and impairs the agreement between the theoretical and experimental values.[111]

For organic compounds containing the thiodiimide group, non-empirical quantum-chemical calculations have not been made. According to a calculation by the CNDO/2 method with inclusion of the 3*d* AO of sulphur in the basis set, the sulphur atom in dimethylthiodiimide has an effective positive charge of 0.21 e, induced, according to the analysis of the orbital populations, by the SN π-bond.[94] According to Grunwell and Danison,[112] in the CNDO/2 calculations for *NN'*-dimethylthiodiimide and the hypothetical *NN'*-dihydrothiodiimide, the effect of the inclusion of the 3*d* AO of sulphur in the basis set is expressed predominantly by the achievement of a satisfactory agreement between the SN bond lengths and the experimental values and by the stabilisation of the planar conformation via the so-called π' bonding. The inclusion of the 3*d* AO of sulphur does not influence the symmetries of the HOMO and the LUMO, but the geometrical isomerism does affect the symmetry of the HOMO.[113]

According to a calculation in terms of the CNDO/2 approximation, without taking into account the 3*d* AO of sulphur,[110] the distribution of electron density within the limits of the NSN fragment of diphenylthiodiimide is ylide-like but with a considerable amount of SN double bond character, which can be reproduced by a superposition of structures (2) while the valence state of the sulphur atom is intermediate between its state in the thiocarbonyl group and in the thiophen molecule. In relation to the benzene ring, the thiodiimide group in the ground state of the molecule may behave as a weak π donor.[110]

According to the same calculation,[110] the order of the SN π-bond in diphenylthiodiimide is 0.659. The study of the π-bond orders in dimethylthiodiimide and heterocycles containing the N=S=N groups such as naphtho[1,8,*cd*]-1,2,6-thiadiazine, benzo-2,1,3-thiadiazole and 2,1,3-thiadiazole in terms of the CNDO/2 approximation, with and without the inclusion of the 3*d* AO of sulphur in the basis set, has shown that, although there is a definite amount of the SN double bond character in 2,1,3-thiadiazole (the SN π-bond order is 0.428 or 0.379; here and henceforth the first value has been obtained taking into account 3*d* AO of sulphur), its structure is best described by a formula with bivalent sulphur. On passing to benzo-2,1,3-thiadiazole, the amount of the SN double bond character increases, but the SN π-bond order (0.542 and 0.481) is nevertheless lower than in naphtho-[1,8-*cd*]-1,2,6-thiadiazines (0.641 and 0.647) in which it almost agrees with the π-bond order in dimethylthiodiimide (0.651 when account is taken of the 3*d* AO of sulphur). The latter factor can be interpreted as evidence in support of the thiodiimide structure, with quadrivalent sulphur, of naphtho-[1,8-*cd*]-1,2,6-thiodiazine. When the 3*d* AO of sulphur are included in the basis set, the SN π-bond order does not change in this compound, from which it follows that the quadrivalent state of sulphur does not by itself indicate, as is usually assumed, the involvement of the 3*d* AO of sulphur in bonding.[113] Indeed the π-bond in organic thiodiimides, as well as in other heterocumulenes containing quadrivalent sulphur, is described with the aid of MO of the allyl type,[1] made up in the case of thiodiimides of the *p* AO of the nitrogen and sulphur atoms oriented at right angles to the plane of the molecule.

(b) Vibrational spectroscopic data. Special studies[77,114,115] of thiodiimides enriched with ^{15}N have shown that the stretching vibration frequencies of the SN bonds are extremely sensitive to the character of the substituents to which the thiodiimide group is linked (Table 4), but it is difficult to establish general characteristic features. Thus, on passing from dialkyl- to diaryl-thiodiimides, the symmetrical SN stretching vibration frequency falls, while the antisymmetrical frequency increases.[114] The frequency ν_{as}(SN) for dibenzoylthiodiimide is in the range of values for diarylthiodiimides, while ν_s(SN) for the benzoyl derivative is much greater than for aryl derivatives (Table 4). On passing from diaryl- to bis(polyfluoroaryl)-thiodiimides, the stretching vibration frequencies of the SN bond increase, which probably indicates an increase of the SN bond force constants and orders as a consequence of the weakening of the p_π–p_π interaction between NSN and the polyfluoroaryl group compared with the aryl group.[115]

Table 4. Vibration frequencies (cm^{-1}) of the thiodiimide group in the compounds R–N=S=N–R.

R	ν_{as}(SN)		ν_s(SN)		δ(NSN)		Refs.
	IR	Raman	IR	Raman	IR	Raman	
Alk	1192–1218	1189–1216	1055–1096	1056–1082	—	—	[114]
Me_3Si	1261	1261	1140	1140	435	436	[88]
Ar	1252–1300	1250–1293	958–980	960–984	778–804	792–804	[114]
Ar_f	1445*	1430–1450	**	1160–1205	845–855	854–862	[115]
PhCO	1275	—	1170	—	—	—	[77]

*The position of the band is difficult to determine owing to its overlap with the bands due to the polyfluoroaryl group.[115]
**Absent from the infrared spectrum.[115]

On excitation of the Raman spectrum of di-*p*-tolylthiodiimide by radiation at a wavelength of 458 nm (the maximum of the long-wavelength absorption in the electronic spectrum of this compound is at 434 nm[51]), a resonance increase in the intensities of all the bands occurs in the range 700–1400 cm^{-1},

which indicates an effective delocalisation of the π-bonding in the molecule. The intensities of the ν_s(SN) and ν_s(PhN) bands increase to the greatest extent, which indicates that the long-wavelength absorption band in the electronic spectrum of di-*p*-tolylthiodiimide is associated with a transition accompanied by an appreciable redistribution of charge between the N=S=N group and the aromatic rings.[114] This observation agrees well with the results of a theoretical interpretation of the electronic spectra of diarylthiodiimide[110] (see previous Section).

The substituents X in the compounds 4-$O_2NC_6H_4N$=S=NC_6.H_4X-4 decrease the symmetrical stretching vibration frequency of the nitro-group in their infrared spectra, while electron-accepting substituents behave in different ways—they either decrease or increase the frequency, $\Delta\nu$ being in no way correlated with the Taft constant. This led to the conclusion[109] that there is no direct transmission of the effect of the conjugation of the substituent X to the second ring via the thiodiimide group and that an interaction of this kind is limited to the sulphur atom.

From the relation between the antisymmetrical stretching vibration frequency of the nitro-group and the constant σ_p^0, the σ_p^0 for the 4-$O_2NC_6H_4N$=S=N and C_6H_5CON=S=N groups were calculated from the IR spectroscopic data for bis(4-nitrophenyl)- and *N*-benzoyl-*N'*-4-nitrophenyl-thiodiimides as 0.2 and -0.3 respectively, from which it follows that the first group is electron-accepting and the second is electron-donating in relation to the benzene ring.[78]

The inductive influence of the C_6H_5N=S=N group has been estimated from the IR spectrum of *N*-benzenesulphonyl-*N'*-phenylthiodiimide on the basis of the finding that the average stretching vibration frequency of the SO_2 group is sensitive mainly to *I* effects.[78] It was assumed that $\nu_s(SO_2)$ and $\nu_{as}(SO_2)$ are 1164 and 1248 cm^{-1} respectively. The frequency $\nu_s(SO_2)$ = 1164 cm^{-1} agrees with the results of other studies dealing with the IR spectra of *N*-arenesulphonyl-*N'*-aryl- or bis(arenesulphonyl)-thiodiimides,[65,109] but the frequency $\nu_{as}(SO_2)$ = 1248 cm^{-1} disagrees with these results. According to Wucherpfennig and Kresze,[65] $\nu_{as}(SO_2)$ in the IR spectra of thiodiimides of the type $(R-SO_2-N=)_2S$ is in the range 1340–1355 cm^{-1}, while according to Lutskii et al.[109] the band at 1330 cm^{-1} in the spectrum of *N*-benzenesulphonyl-*N'*-phenylthiodiimide is associated with $\nu_{as}(SO_2)$. The conclusion[78] that $\sigma_I \cong 0.2$ for the C_6H_5N=S=N group becomes controversial as a result of this finding.

The vibrational spectra of compounds with sulphur–nitrogen chains longer than N=S=N have not been studied systematically. If the known group frequencies of the F_3CS fragment are excluded from the IR spectrum of bis(trifluoromethanesulphonyl)thiodiimide, we find that ν_{as}(NSN) = 940 cm^{-1}, ν_s(NSN) = 651 cm^{-1}, and δ(NSN) = 503 cm^{-1}.[116] The explanation of such a marked decrease of the frequencies is based on the concept of the pulsation of the entire SNSNS fragment, in which mainly nitrogen vibrates as a consequence of the large difference between the masses and the π-electron system of the central (multiple) SN bonds extend over the entire sulphur–nitrogen skeleton, which equalises the bond orders to 1.5. The appreciable decrease of the ν_{as}(SN) frequency on passing from ArSN=S=N–$SiMe_3$ (ν_{as} = 1194–1202 cm^{-1}) to $(ArSN=)_2S$ (ν_{as} = 1138–1146 cm^{-1}) and $(ArSN=S=N)_2S$ (ν_{as} = 1080–1100 cm^{-1}) has been explained analogously.[2] An alternative explanation is associated with the possible difference between the molecular geometries: if bis(arenesulphonyl)thiodiimides have the *cis,cis*-geometry, then *N*-arenesulphenyl-*N'*-trimethylsilylthiodiimides are most likely to have the *cis,trans*-geometry.[2]

The concept of the decrease of the SN vibration frequency is a consequence of the increased electron delocalisation in the sulphur–nitrogen chain with increase of its length appears attractive but apparently agrees poorly with structural data. On passing from diaryl- to bis(arenesulphenyl)-thiodiimides, the lengths of the bonds in the central N=S=N units hardly change and the complete equalisation of the π-bonds suggested by Haas and Schott[116] does not exist (see above).

(c) ^{15}N NMR spectroscopic data. In this Section all the chemical shifts quoted in the original studies relative to different standards have been recalculated in relation to nitromethane; the positive values correspond to upfield shifts.

The ^{14}N NMR signal of diphenylthiodiimide (solution in ether) is at ~72 p.p.m.,[117] whereas the ^{15}N NMR signal is at ~114 p.p.m. [solution in dimethyl sulphoxide (DMSO)] according to other data.[102] It is known that, within the limits of experimental error, the chemical shifts are the same for the ^{14}N and ^{15}N nuclei when the spectra are recorded under identical conditions.[118] The discrepancy between the results of Yavari et al.[102] and Mason et al.[117] is too great to be caused by the difference between the solvents, the chemical shift quoted for nitrogen in diphenylthiodiimide in these investigations is clearly erroneous. Since it is known[119–121] that certain thiodiimides interact with DMSO, the result of Mason et al.[117] appears to be less reliable.

Comparison with the closest analogues, namely *N*-sulphinylarylamines, has shown that the NMR signals of nitrogen in the spectra of diarylthiodiimides are located in a somewhat higher field. For example, the ^{14}N NMR signal of diphenylthiodiimide has undergone an upfield shift relative to the signal of *N*-sulphinylaniline by approximately 18 p.p.m.[117,122] It is of interest to note that the chemical shift of the ^{14}N NMR signal in the spectrum of diphenylthiodiimide is the same as that of pyrimidine.[117]

On passing from diphenylthiodiimide to *N*-pentafluorophenyl-*N'*-phenylthiodiimide and further to bis(pentafluorophenyl)thiodiimide, the ^{15}N NMR signal undergoes an upfield shift.[50] Analogous shifts on passing from hydrocarbon analogues to perfluorinated derivatives are observed also for many other classes of aromatic nitrogen-containing compounds.[50,123,124] Comparison of ^{15}N NMR and S K_β spectroscopic data for thiodiimides has shown that the chemical shift of the nitrogen signal is influenced primarily by the changes in the character of the interaction of the nitrogen atom with aromatic rings and not with sulphur atoms.[50] According to a calculation in terms of the CNDO/2 approximation[110] and ^{13}C NMR data,[125] the thiodiimide group is electron-donating in relation to the benzene ring ($\sigma^+ = -0.1$ for the C_6H_5N=S=N group[125]). The weakening of the p_π–p_π interaction of the NSN group and the aromatic rings on passing from diaryl- to bis(polyfluoroaryl)-thiodiimides[50,115] therefore entails an increase of π-electron density at the nitrogen atom. An increase of electron density (negative charge) on the nitrogen atom leads to a decrease of the absolute value of the paramagnetic term in the expression for the shielding constant and hence to an increase of the shielding and an upfield shift of the ^{15}N NMR signal.[118]

Table 5. The constants σ_R^0 and σ_I of complex substituents R containing the thiodiimide group.*

R	σ_R^0	σ_I	R	σ_R^0	σ_I
C_6F_5NSN	−0.03	−0.16	C_6H_5NSNS	0.01	0.17
C_6H_5NSN	−0.11	−0.14	C_6F_5SNSNS	0.02	0.22
C_6F_5SNSN	−0.21	−0.10	C_6H_5SNSNS	−0.03	0.13
C_6H_5SNSN	−0.16	−0.04	t-BuNSN	−0.48	0.73
C_6F_5NSNS	0.10	−0.08			

*According to the data of Brands and Golloch.[127]

Apart from the effective atomic charge, the chemical shifts of nitrogen depend on the average energy ΔE of the electronic excitations which correspond to the circulation of the electron around the nucleus when the electron is described by a point charge. In this case the lower ΔE, the greater the deshielding. The energy ΔE can be estimated from the energy of the long-wavelength bands in the electronic absorption spectra associated with the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions.[123] The additional stabilisation of the σ MO of planar molecules or groups relative to π MO when the hydrogen atoms are fully substituted by fluorine (the "perfluoro-effect") leads to a hypsochromic band shift in the electronic absorption spectra caused by the $\sigma \rightarrow \pi^*$ and $n \rightarrow \pi^*$ excitations.[123,126] On passing from diphenyl- to bis(pentafluorophenyl)-thiodiimide, the long-wavelength absorption band in the electronic spectrum shifts towards shorter wavelengths (Table 3). This band is usually attributed to $\pi \rightarrow \pi^*$ excitations[110,111] but in the spectra of diaryl- and bis(polyfluoroaryl)-thiodiimides it is fairly broad and apparently can mask the band associated with the $n \rightarrow \pi^*$ excitations. If this is indeed so, on passing from diphenyl- to bis(pentafluorophenyl)thiodiimide, ΔE increases, which also leads to an upfield shift of the ^{15}N NMR signal.

(d) Data obtained by other methods. The constants σ_R^0 and σ_I presented in Table 5 have been calculated from the ^{19}F NMR spectroscopic data for thiodiimides containing the pentafluorophenyl substituent.[127]

Compounds of the type $C_6H_5SO_2N{=}S{=}NC_6H_4X\text{-}4$, $4\text{-}O_2NC_6H_4N{=}S{=}NC_6H_4X\text{-}4$, $(ArN{=})_2S$, and $C_6H_5CON{=}S{=}NAr$ have been investigated by the method of dipole moments.[18,109] The results were interpreted on the assumption that the molecules exist either in the *cis,cis*-configuration[109] or *trans,trans*-configurations.[78] However, thiodiimides with aromatic substituents exist in solution in the form of an equilibrium mixture of the *cis,trans*- and *trans,trans*-isomers with the *cis,trans*-isomer predominating.[48] This finding casts doubt on the conclusions[78,109] based on the study of the dipole moments.

In the mass spectrum of the *N*-pentafluorophenyl-*N'*-phenylthiodiimides the peaks of the $C_6F_5N^+$ and $C_6H_5NS^+$ ions predominate over the peak of the $C_6F_5NS^+$ ion. Such fragmentation is explained by the powerful polarising action of the pentafluorophenyl group, which weakens one of the sulphur–nitrogen bonds in accordance with the scheme[128]

$$Ph_f{-}N{=}S{=}N{-}Ph \longleftrightarrow Ph_f{-}\bar{N}{-}\overset{+}{S}{=}N{-}Ph \dashrightarrow \xrightarrow[-2e^-]{+e^-} Ph_f{-}\dot{N}{-}\overset{+}{S}{=}N{-}Ph\,.$$

IV. CHEMICAL PROPERTIES

The most characteristic reactions of organic compounds containing the thiodiimide group are those with nucleophiles and cycloaddition. The reactivity of the N=S=N fragment depends significantly on the character of the groups linked to it and as a rule decreases with increasing electronegativity of the latter. According to frontier orbital theory, in the reactions of nucleophiles with electrophiles (in the given case with thiodiimides) the interaction of the HOMO of the nucleophile with the LUMO of the electrophile is most important.[129] However, the excited states of the molecules of organic thiodiimide have been scarcely investigated. Different conclusions about the true mechanisms of many reactions with their participation are therefore at present hardly possible. In particular, one cannot rule out the possibility that not all reactions with what are formally nucleophiles do indeed involve nucleophilic attack on the sulphur atom of the thiodiimide group. It is extremely likely that many reactions of thiodiimides proceed with the intermediate participation of thionitroso-compounds.

It has been shown for a large number of examples[130] that the chemical properties of organic thiodiimides are close to those of sulphur dioxide and *N*-sulphinylamines. At first sight, this is entirely natural, since both thiodiimides and *N*-sulphinylamines are aza-analogues of SO_2. On the other hand, it has been shown that the positive charges on the sulphur atoms and the distribution of the 3*p* electrons of sulphur among the MO are appreciably different for SO_2, *N*-sulphinylarylamines, and thiodiimides with aromatic substituents at the nitrogen atom.[131] Hence, one may imagine that the properties of the excited states can also differ and one should therefore expect some differences in reactivity. The latter do indeed exist. For example, whereas tris(trimethylstannyl)amine forms an adduct with bis(pentafluorophenyl)-thiodiimide,[132] in its reaction with *N*-sulphinylpentafluoroaniline it forms *NN*-bis(trimethylstannyl)pentafluoroaniline and trimethylstannylthionylimide.[83]

1. Thermolysis

Dimethylthiodiimide decomposes slowly even at room temperature.[16,17] The t-alkyl derivatives are more stable. The pyrolysis of di-t-butylthiodiimide at 265 °C results in a 60% yield of isobutene. The reaction is apparently concerted. The pyrolysis of diphenylthiodiimide at 200 °C affords azabenzene with a 66% yield.[133] It has been suggested that this reaction takes place with participation of a thiadiazirine intermediate.[113] The thermolysis of bis(2,4-di-t-butyl-6-methylphenyl)thiodiimide in boiling benzene leads to the corresponding arylamine and benzothiazole.[59]

2. Interaction with Nucleophiles

All organic thiodiimides tend to hydrolyse; the hydrolysis products are the corresponding amines or amides and sulphur dioxide. Bis(arylsulphenyl)thiodiimides, whose hydrolysis leads to arenethiols, sulphur dioxide, and ammonia are an exception.[134] The hydrolytic stability of thiodiimides decreases with enhancement of the electron accepting properties of the substituents at the N=S=N groups. Thus bis(arenesulphinyl)- and bis(alkoxycarbonyl)-thiodiimides are readily hydrolysed even by atmospheric moisture,[64,79] while bis(pentafluorophenyl) thiodiimide hydrolyses faster by more than an order of magnitude than bis(4-chlorophenyl)-thiodiimide under identical conditions.[49]

The interaction of bis(benzenesulphonyl)thiodiimide with aliphatic alcohols yields esters of *NN'*-bis(benzenesulphonyl)-amidoiminosulphurous acid.[135] Ditosylthiodiimide interacts analogously with benzyl alcohol and oximes. In this case the esters formed are unstable and decompose giving rise to the final reaction products:[136]

$$(TosN{=})_2S \begin{cases} \xrightarrow{PhCH_2OH} TosN{=}S(HNTos)OCH_2Ph \rightarrow \\ \qquad \rightarrow TosNSO + PhCH_2NHTos; \\ \xrightarrow{PhCH{=}NOH} TosN{=}S(HNTos)ON{=}CHPh \rightarrow \\ \qquad \rightarrow TosNSO + TosNH_2 + PhCN; \\ \xrightarrow{Ph_2C{=}NOH} TosN{=}S(HNTos)ON{=}CPh_2 \rightarrow \\ \qquad \rightarrow TosNSO + PhC(=NPh)HNTos. \end{cases}$$

Ditosylthiodiimide interacts with aliphatic sulphides, including cyclic sulphides, as nucleophiles. The products are the corresponding *SS*-dialkyl-*N*-tosylsulphimines and elemental sulphur.[137]

Bis(arenesulphonyl)thiodiimides react with compounds containing the O=X bond (X = C, S, P, or As):[120]

$$(ArSO_2{-}N{=})_2S \xrightarrow{-SO_2}$$

$\xrightarrow{Ar'CHO}$ $Ar'CH{=}N{-}SO_2Ar$;

$\xrightarrow{PhCONMe_2}$ $PhC(=N{-}SO_2Ar)NMe_2$;

$\xrightarrow{HCONMe_2}$ $Me_2NCH{=}N{-}SO_2Ar$;

$\xrightarrow{Me_2SO}$ $Me_2S{=}N{-}SO_2Ar$;

$\xrightarrow{R_3PO}$ $R_3P{=}N{-}SO_2Ar$;

$\xrightarrow{Ph_3AsO}$ $Ph_3As{=}N{-}SO_2Ar$;

R=Me, Et, Ph.

Dibenzoylthiodiimide reacts analogously with DMSO.[121] The interaction apparently begins with nucleophilic attack by the O atom of the O=X group on the S atom of the thiodiimide group:

$$(ArSO_2N{=})_2S \xrightarrow{R_nX{=}O} \left[\begin{array}{c} ArSO_2\bar{N}{-}S{=}NSO_2Ar \\ | \\ R_n\overset{+}{X}{-}O \end{array}\right] \rightarrow$$

$$\rightarrow \left[\begin{array}{c} ArSO_2N{-}S{=}NSO_2Ar \\ | \quad | \\ R_nX{-}O \end{array}\right] \xrightarrow{-R_nX{=}NSO_2Ar}$$

$$\rightarrow [ArSO_2{-}NSO] \xrightarrow[-SO_2]{R_nX{=}O} R_nX{=}NSO_2Ar .$$

In those cases where the intermediate *N*-sulphinylamine does not react with the oxygen-containing compound, the reaction stops in the first stage. For example, the interaction of *N*-benzenesulphenyl-*N'*-phenylthiodiimide with DMSO results in the formation of *N*-benzenesulphenyl-*SS*-dimethylsulphimine and *N*-sulphinylaniline.[120] The reaction of ditosylthiodiimide with sulphoxides leads to similar products, namely *SS*-disubstituted *N*-tosylsulphimines and *N*-sulphinyltoluene-*p*-sulphonamide. The conversion of chiral sulphoxides into sulphimines in different solvents proceeds via different mechanisms. In pyridine at 0 °C the reactions are termolecular and proceed with inversion of the configuration at the sulphur atom; in benzene the reactions take place with retention of the configuration and are bimolecular.[119]

The reactivity of thiodiimides with respect to compounds having an O=X bond decreases with decreasing electronegativity of the substituents at the nitrogen atom. Thus diarylthiodiimides containing nitro-groups or chlorine atoms in the 4,4'-positions in the rings react with aldehydes like the bis(arenesulphonyl)derivatives, while diphenylthiodiimide and diarylthiodiimides containing electron-donating substituents do not react with aldehydes, sulphoxides, and phosphine oxides.[120]

Dibenzoylthiodiimide does not react with aromatic aldehydes, but in the presence of benzamide the reaction proceeds readily with formation of *NN'*-diaroylamidals. The thiodiimide behaves simultaneously as a dehydrating agent and an additional source of the amide:[121]

$$ArCHO + PhCONH_2 + (PhCON{=})_2S \xrightarrow{-SO_2} ArCH(NHCOPh)_2$$

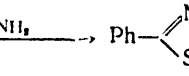
Dibenzoylthiodiimide reacts with trichloroacetaldehyde to form *NN'*-diacetylchloral amidal. In the presence of aluminium chloride, the reaction leads to *N*-benzoylchloral imine.[121]

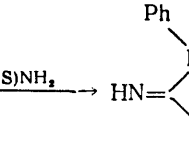
Phosphine sulphides and dialkylthioamides of carboxylic acids react with bis(arenesulphonyl)thiodiimides like the corresponding oxygen-containing compounds to form phosphazo-compounds or amidines. On reaction with bis(arenesulphonyl)thiodiimides, thiobenzamide and phenylthiourea are converted into 1,2,4-thiadiazole and 1,2,4-thiadiazolidine derivatives:[120]

$$(ArSO_2N{=})_2S{-}$$

$\xrightarrow{R_3P{=}S}$ $R_3P{=}NSO_2Ar$;

$\xrightarrow{RC(=S)NR_2}$ $RC(=NSO_2Ar)NR_2$;

$\xrightarrow{PhC(=S)NH_2}$  ;

$\xrightarrow{PhHNC(=S)NH_2}$ 

NN-Dibenzoylarenesulphonamides and arenesulphonylphthalimides have been obtained respectively on heating bis(arenesulphonyl)thiodiimides with benzoic or phthalic anhydride.[120]

The reaction of bis(benzenesulphonyl)thiodiimide with dialkylamines results in the formation of dialkylammonium salts. The *NN*-dialkylamides of *N'N''*-bis(benzenesulphonyl)-amidoiminosulphurous acid are probably formed in the first stage. They have acid properties and react with a second dialkylamine molecule.[135] *N*-Aryl-*N'*-benzenesulphonylthiodiimides are symmetrised in the presence of secondary amines; the symmetrisation is accompanied by the formation of the dialkylammonium salts from the bis(benzenesulphonyl) derivative:[135]

$$PhSO_2{-}N{=}S{=}N{-}Ar \xrightarrow{Alk_2NH} (ArN{=})_2S +$$

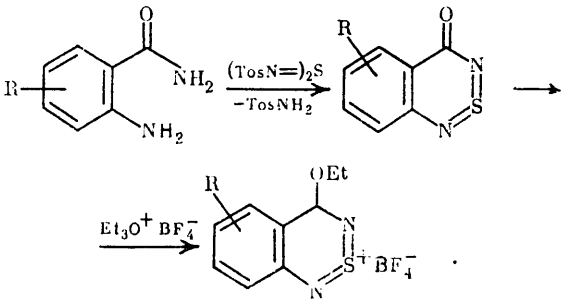
$$[(PhSO_2N)_2SNAlk_2]^- [Alk_2NH_2]^+ .$$

Tris(trimethylstannyl)amine and some of its derivatives add to bis(polyfluoroaryl)- and bis(arenesulphonyl)-thiodiimides in equimolar proportions:[132]

$$(R{-}N{=})_2S \xrightarrow{(Me_3Sn)_2NR'} \begin{array}{l} Me_3SnN\diagup R \\ \qquad\quad \diagdown S{=}NR' \\ Me_3SnN\diagup R \end{array} ;$$

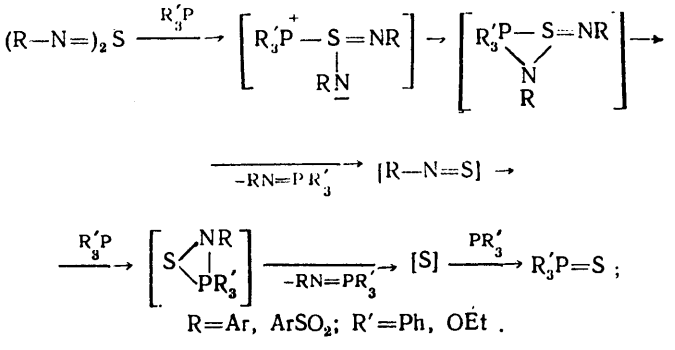
R=C_6F_5, R'=Me_3Sn, Me, C_6F_5; R=4-$ClC_6H_4SO_2$, R'=Me.

The interaction of thiodiimides with aromatic amines was examined above (see Section II). The reaction of bis(benzenesulphonyl)thiodiimide with *o*-phenylenediamine leads to benzo-2,1,3-thiadiazole.[61] Substituted 2-amino-benzamides interact with ditosylthiodiimide to form cyclic products whose alkylation gives rise to benzo-2,1,3-thiadiazinium salts:[138]

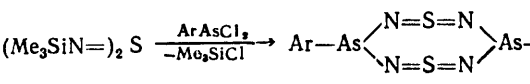


Bis(arenesulphonyl)- and diaryl-thiodiimides react with phosphines and phosphites. The interaction of bis(arenesulphonyl)thiodiimides and diarylthiodiimides containing electron-accepting substituents in the ring with triphenylphosphine leads to triphenylphosphine sulphide and phosphazo-compounds.[120] On heating with triphenylphosphine, *N*-t-butyl-*N'*-trimethylsilylthiodiimide decomposes analogously to the corresponding iminophosphoranes and phosphine sulphide.[33] The reactivity of thiodiimides towards phosphines diminishes with increasing electronegativity of the substituents at the nitrogen atoms. Thus triphenylphosphine reacts exothermically with bis(arenesulphonyl)thiodiimides, while the reaction with bis(4-nitrophenyl)thiodiimide takes place only on heating. Diarylthiodiimides containing electron-donating substituents do not react with triphenylphosphine.[120]

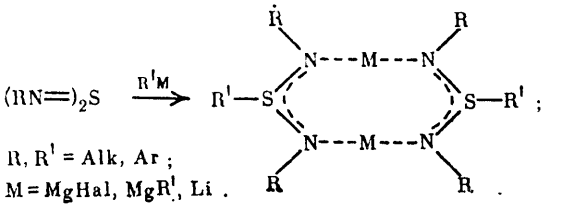
The interaction of bis(arenesulphonyl)- and diaryl-thiodiimides with phosphites is accompanied by the formation of phosphorothioates and phosphazo-compounds.[43,120] The initial stage of the reaction of bis(arenesulphonyl)- and diarylthiodiimides with phosphines and phosphites apparently consists in the nucleophilic attack by the phosphorus atom on the sulphur:[43,120]



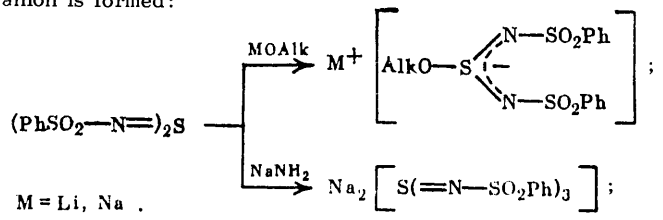
The reaction of triphenylphosphine with dibenzoylthiodiimide takes place differently and leads to benzonitrile, elemental sulphur, and triphenyl-phosphine oxide.[121] The interaction of bis(trimethylsilyl)thiodiimide with phenyl- and mesityl-dichloroarsines leads to the corresponding dithiatetrazadiarsocines:[139]



Organomagnesium and organolithium compounds add quantitatively to dialkyl- and diaryl-thiodiimides. This reaction has been used as the basis of a convenient method for the quantitative analysis of organometallic compounds:[140]

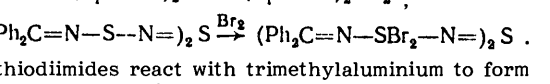


Bis(arenesulphonyl)- and bis(trifluoromethanesulphonyl)-thiodiimides react with lithium and sodium alkoxides to form stable salts of anions and contain a tricoordinate sulphur atom according to X-ray diffraction data. The interaction with dry CsF proceeds analogously. When bis(benzenesulphonyl)thiodiimide is treated with sodium amide, a stable salt containing the tris(benzenesulphonylimido)sulphide anion is formed:[141]



3. Interaction with Electrophiles

When thiodiimides are allowed to react with fluorine, the *SS*-difluoro-derivatives are obtained.[142] Bromination of 1,5-bis(diphenylmethyleneamino)trithiodinitride takes place apparently in the 1,5-positions in the sulphur–nitrogen fragment:[69]

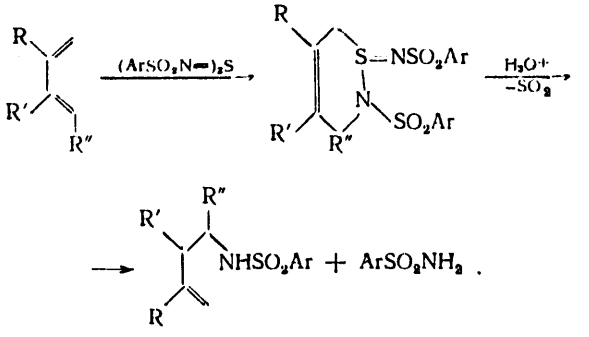


Diarylthiodiimides react with trimethylaluminium to form complexes of the type $\{Me_2Al[ArNS(Me)NAr]\}_2$, in which the sulphur atom is methylated.[143]

4. Cycloaddition Reactions

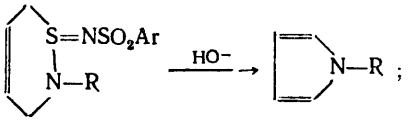
Organic thiodiimides are capable of undergoing the $[4\pi + 2\pi]$ and $[2\pi + 2\pi]$-cycloaddition reactions. The former are represented by the 1,4-cycloaddition to 1,3-dienes and the 1,3-cycloaddition to diphenylketen and the latter by the 1,2-cycloaddition to heterocumulenes and olefins.

Bis(arenesulphonyl)thiodiimides react exothermically with 1,3-dienes at room temperature to form 1-arenesulphonyl-imino-2-arenesulphonyl-3,6-dihydro-1,2-thiazines.[64,65,144] Acid hydrolysis of the adduct affords arenesulphonamides, sulphur dioxide, and arenesulphonyliminobut-3-enes:[144]



Bis(alkoxycarbonyl)- and diaroyl-thiodiimides react analogously with dienes.[77,79]

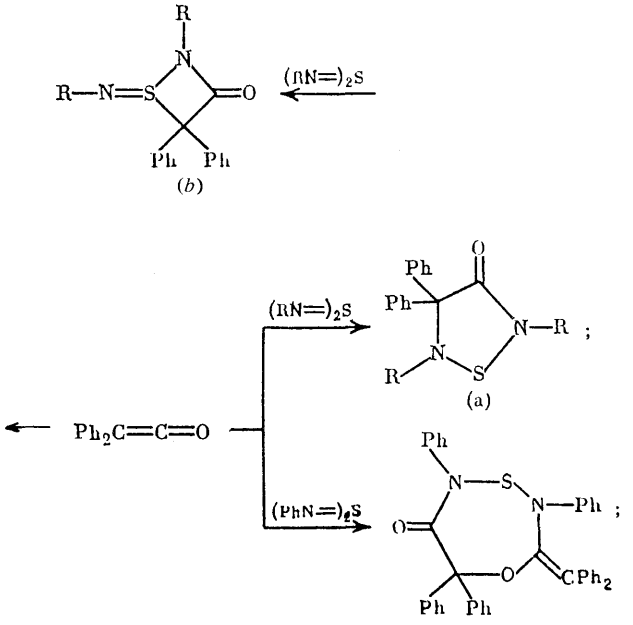
Asymmetric thiodiimides having non-equivalent SN bonds, for example *N*-alkyl- and *N*-aryl(heteryl)-*N'*-arenesulphonylthiodiimides react only via the SN bond remote from the sulphonyl group.[63,80,145] Acid hydrolysis of thiazines proceeds in the same way as for 2-arenesulphonyl- and 2-alkoxycarbonyl-derivatives, but treatment of 1-arenesulphonylimino-2-aryl(heteryl)-3,6-dihydro-1,2-thiazines with an alcoholic solution of alkali makes it possible to obtain *N*-arylpyrroles[145] and 2-(1-pyrrolyl)pyridines:[63]



R=Ar, 2-Py .

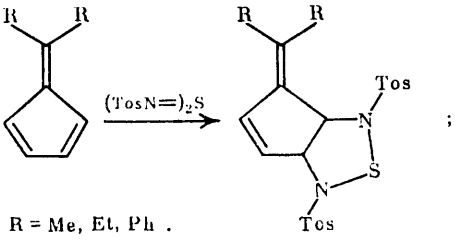
The rate of reaction of thiodiimides with 1,3-dienes depends on the character of the substituent at the nitrogen atom. Whereas bis(arenesulphonyl)thiodiimides react with evolution of heat, *N*-aryl-*N'*-arenesulphonylthiodiimides react only on heating. Electron-accepting substituents in the aryl group accelerate the reaction, while electron-donating substituents retard it.[145] Dialkyl-, diaryl-, and *N*-alkyl-*N'*-bromo-, and *N*-benzenesulphenyl-*N'*-benzenesulphonyl-thiodiimides do not enter into the cycloaddition reaction with 1,3-dienes.[18,68,80]

Ditosyl-, diphenyl, and bis(4-ethoxycarbonylphenyl)-thiodiimides react with diphenylketen at 70–80 °C to form 1,3-adducts with reduction of sulphur(IV) to sulphur(II)—2,5-diaryl[bis(arenesulphonyl)]-3,3-diphenyl-1,2,5-thiadiazolidin-4-ones are formed.[146–148] At −15–0 °C the reaction of diphenylketen with ditosylthiodiimide and di-t-butylthiodiimide proceeds as 1,2-cycloaddition,[146,148] while the reaction with diphenylthiodiimide at 6–8 °C results in the formation of perhydro-2-diphenylmethylene-3,5,7,7-tetraphenyl-1,4,3,5-oxathiadiazepin-6-one, whose structure has been confirmed by X-ray diffraction:[148]



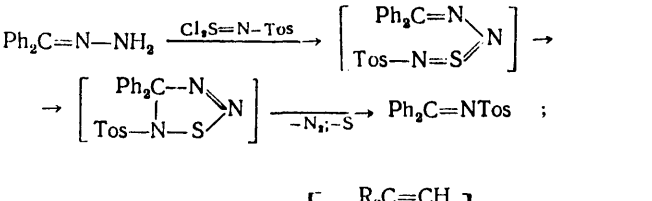
(a) R = Tos, Ph, 4-EtOCOC$_6$H$_4$;
(b) R = Tos, t-Bu.

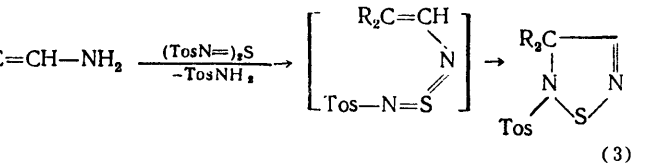
Di-t-butylthiodiimide reacts with dichloroketen at 70 °C to form a 1,2-cycloaddition product.[149] Dialkyl- and diarylthiodiimides react with bis(trifluoromethyl)thioketen to form the corresponding keten imines. No data confirming the mechanism have been obtained, but one cannot rule out the possibility that the reaction proceeds via five- or four-membered rings—the products of the initial cycloaddition of the thiodiimides.[150] Ditosylthiodiimide enters into a 1,3-cycloaddition reaction with 6,6-disubstituted fulvenes at −10–−15 °C:[151]



R = Me, Et, Ph .

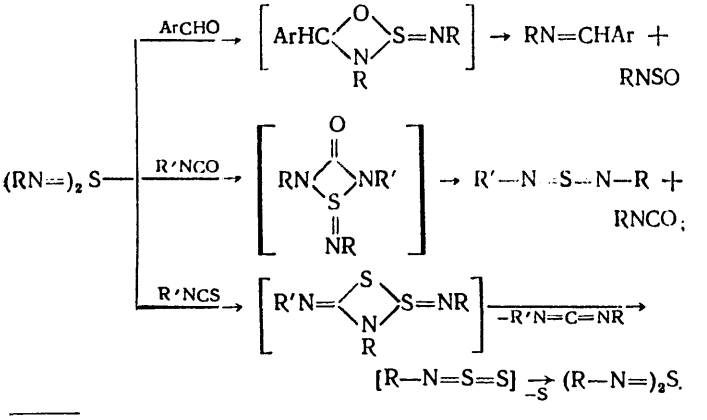
An unusual intramolecular 1,3-cycloaddition of the thiodiimide group to the azomethine bond probably takes place in the reaction of *SS*-dichloro-*N*-tosylsulphimine with benzophenone hydrazone, which leads to a Schiff base, elemental nitrogen, and sulphur.[152] The reaction [153]





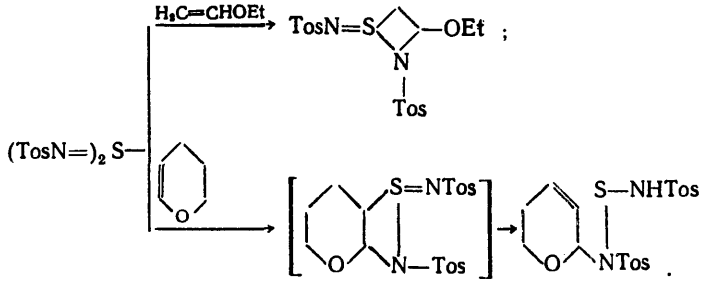
(3)

probably includes the transamination and intramolecular cycloaddition stages. Certain reactions of di-t-butylthiodiimide, such as those with aldehydes,§ isocyanates, and isothiocyanates probably proceed via the [2π + 2π]-cyclo-addition stage. The cyclic adducts decompose in such a way that fragment exchange reactions are observed ultimately:[154]

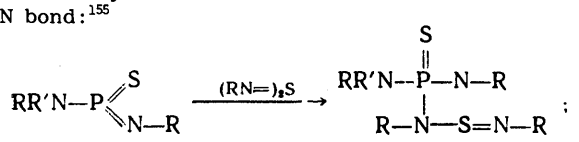


§ Levchenko and Ugarov[120] regard this reaction as nucleophilic (see Subsection 2).

Yet another example of 1,2-cycloaddition is provided by the reaction of ditosylthiodiimide with "electron-rich" olefins (vinyl ethers):[1,137]

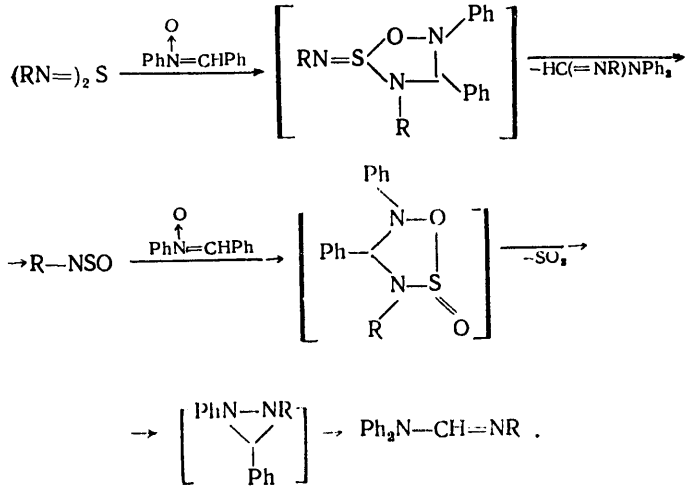


It is of interest to note that thiodiimides undergo 1,2-cycloadditon not only to a carbon–carbon double bond but also to a P=N bond:[155]

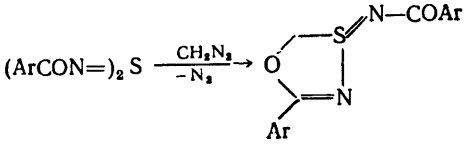


R = t-Bu, R′ = Me_3Si .

Bis(arenesulphonyl)- and dibenzoyl-thiodiimides readily react with *CN*-diphenylnitrone to form respectively *N*-arenesulphonyl-*N′N′*-diphenylformamidines[120] and *N*-benzoyl-*N′N′*-diphenylformamidines.[121] One cannot rule out the possibility that the reaction begins with 1,3-dipolar cycloaddition of the nitrone at the thiodiimide group and involves subsequent decomposition of the adduct:



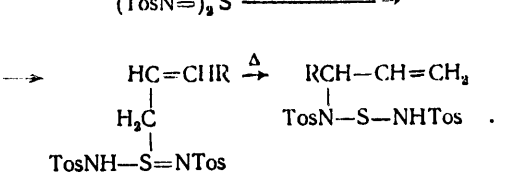
The reaction of diaroylthiodiimides with diazomethane, leading to 3-aroylimino-5-aryl-1,3,4-oxathiazolines,[156] probably includes cheletropic cycloaddition of singlet carbene to the quasi-buta-1,3-diene system formed by the C=O and S=N bonds of the initial thiodiimide:



Theoretical study of the cycloaddition reactions of thiodiimides has shown that the thermal 1,4- and 1,3-cycloaddition reactions are symmetry-allowed; the 1,2-cycloaddition is symmetry-allowed only for the *cis,trans*-isomer and can take place via the overlap of the HOMO of the thiodiimide and the LUMO of the olefin.[113]

5. The Ene Synthesis

Ditosylthiodiimide reacts with many alkenes to form allylsulphinamides capable of undergoing a 2,3-sigmatropic rearrangement on further heating:[119,157,158]

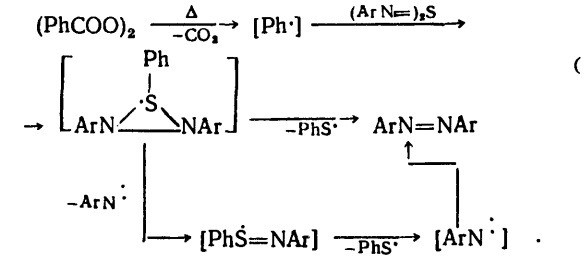


The relative reactivities of ene compounds and the regio- and stereo-selectivity of the reaction have been studied in detail.[158] The preparative application of this reaction for the synthesis of primary allylamines has been examined in a review.[159]

6. Interaction with Free Radicals

Di-t-butylthiodiimide readily combines with radicals of the type $R_n\dot{M}$ [for example, $F_3\dot{C}$, $Me_3\dot{S}i$, $(n\text{-}Bu)_3\dot{S}$, $F_3C\dot{S}$, and $(EtO)_2\dot{P}O$] with formation of the relatively stable nitrogen-centred radical t-Bu$\dot{N}$SN(Bu-t)MR_n.[160]

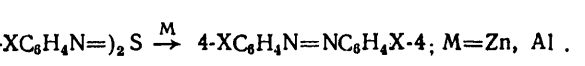
The interaction of diarylthiodiimides with the phenyl radical proceeds differently when equimolar amounts of benzoyl peroxide and the thiodiimide are refluxed in benzene. The reaction leads to biphenyl, diphenyl disulphide, and the corresponding azo-compound. The mechanism proposed for it is illustrated in Scheme (4). Arylnitrenes also participate in the reaction to a slight extent:[161]



(4)

7. Elimination of Sulphur by Metals

The reaction of diphenylthiodiimide with metals leads to azobenzene, probably via an intramolecular pathway, since a mixture of analogues (with X=X and X=Ph in the Scheme presented below) gives rise to azobenzene and 4,4′-diphenylazobenzene; 4-phenylazobenzene is not then formed:[41]



8. Oxidation

When *N*-2-nitrobenzenesulphenyl-*N'*-tosylthiodiimide was oxidised with lead tetraacetate, potassium permanganate, or selenium dioxide, toluene-*p*-sulphonamide and bis(2-nitrophenyl) disulphide were identified.[68] The interaction of dimethyl- and di-t-butyl-thiodiimides with ozone yielded the corresponding nitroalkanes and *N*-sulphenylalkylamines:[25]

$$(AlkN{=})_2S \xrightarrow{[O_3]} AlkNO_2 + AlkNSO\ .$$

9. Reduction

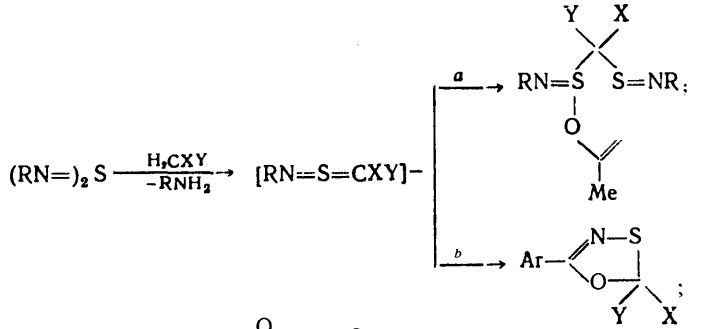
NN'-Bis(arenesulphonyl)-, *NN'*-diaroyl-, and *N*-aryl-*N'*-benzene-sulphonyl-thiodiimides are readily reduced by thiophenols:[136,162]

$$R{-}N{=}S{=}N{-}R' \xrightarrow[-(ArS)_2]{ArSH} R{-}NH{-}S{-}NH{-}R'\ .$$

Ditosylthiodiimide is also reduced to bis(*N*-tosylamino)sulphane by hyrazobenzenes, hydroquinone, catechol, and dihydronaphthalenes—in most cases under mild conditions.[136]

10. Interaction with CH-acids

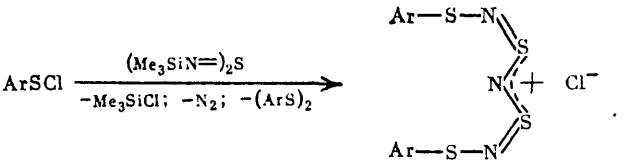
NN'-Bis(arenesulphonyl)thiodiimides react with acetylacetone in acetoacetic and malonic esters in proportions of 1:1 to form 4,6-bis(arenesulphonylimino)-3-oxa-4,6-diathiacyclohex-1-enes.[163] When dibenzoylmethane is treated with bis(benzenesulphonyl)thiodiimide, tetrabenzoylthiirane is obtained,[163] while treatment of 5,5-dimethylcyclohexane-1,3-dione (dimedone) with the same thiodiimide affords compound (I).[164] CH-acids with lower pK_a, for example, malonodinitrile or bis(arenesulphonyl)methanes, do not react with bis(arenesulphonyl)thiodiimides.[163] The reaction of diaroylthiodiimides with acetylacetone, dibenzoylmethane, and dimedone gives rise to 1,3,4-oxathiazole derivatives.[165] It has been suggested[163–165] that *S*-imides are present as intermediates in these reactions:



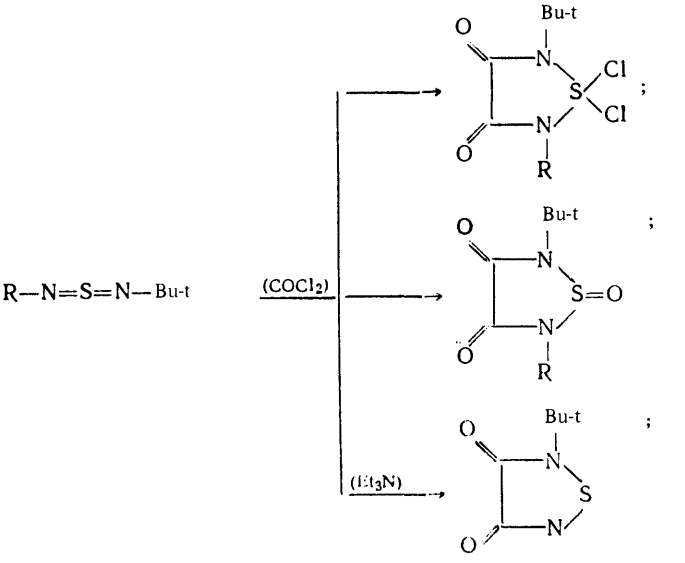
a) R=ArSO$_2$; X=Y=COMe; X=COMe, Y=CO$_2$Et
b) R=ArCO; X=Y=COMe; X=Y=COPh .

11. Other Reactions

Bis(trimethylsilyl)thiodiimide interacts with 4-tolyl- and 4-chlorobenzenesulphenyl chlorides to form the corresponding 1,7-diaryltetrathiotrinitride cations, diaryl disulphide, and molecular nitrogen:[166]



The reaction of thiodiimides with oxalyl chloride in absolute CCl_4 with cooling leads to 1,1-dichloro-2,5-diorganyl-1,2,5-thiadiazolidine-3,4-diones.[167] When the reaction was carried out without cooling, 2,5-diorganyl-3,4-dioxo-1,2,5-thiadiazolidine 1-oxides were obtained, while in the presence of triethylamine the product was 2,5-diorganyl-3,4-dioxo-1,2,5-thiadiazolidines:[168]



R=Ph, t-Bu.

The molecular ions derived from diaryl-, *N*-pentafluorophenyl-*N'*-phenyl-, and bis(pentafluorophenyl)-thiodiimides cyclise according to mass-spectrometric data, losing the *ortho*-substituent in the aromatic ring and forming ions of the benzothiadiazole type with an even number of electrons.[128,169] Diphenylthiodiimide also eliminates sulphur, apparently from the thiadiaziridine isomer of the molecular ion with formation of an azobenzene molecular ion.[128,169] Molecular ions derived from compounds with longer sulphur–nitrogen groups, namely –S–N=S=N– and –S–N=S=N–S–, are fragmented both by the direct cleavage of the sulphur–nitrogen chain and after an intramolecular rearrangement, which leads to the formation of four- and five-membered rings. The contribution of the direct fragmentation increases with increasing length of the sulphur–nitrogen chain. The transition from phenyl derivatives to pentafluorophenyl derivatives has a relatively weak influence on the principal fragmentation reactions, despite the large chemical difference between the C_6H_5 and C_6F_5 groups.[126]

Thus the chemistry of organic compounds containing the thiodiimide group constitute an interesting and developing branch of modern organoelemental chemistry. Further development of this field will probably be associated with the study of compounds containing long acyclic sulphur–nitrogen fragments and also with the synthesis and investigation of the chemical properties of selena- and tellura-analogues of organic thiodiimides, about which little is known at present (see, for example, Refs.121 and 170–172).

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Physicochemical Aspects of the Conversion of Proteins into Food Products

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A general physicochemical approach to the problem of the conversion of protein into food products is examined. The results of studies on processes involving the formation of gels from proteins and polysaccharides—the principal macromolecular components of food—are analysed. The phenomena involving the non-equilibrium formation of complexes by proteins and anionic polysaccharides as well as the limited thermodynamic compatibility in protein-polysaccharide-water and protein-protein-water systems are discussed. The applied aspects of the phenomena indicated are briefly noted.
The bibliography includes 127 references.

CONTENTS

I. Introduction 1025
II. The formation of gels from proteins and polysaccharides 1026
III. Complex formation in solutions of proteins and anionic polysaccharides 1032
IV. Thermodynamic compatibility of proteins and polysaccharides in solution 1034

I. INTRODUCTION

The conversion of proteins and other foods into high quality food products is carried out to ensure a wide-scale application of these substances in man's diet. The preparation of new forms of food (NFF), i.e. food products manufactured by the industrial processing of natural foods, has developed vigorously in recent years.[1] The problem of the economically rational employment of traditional and non-traditional food resources has been solved thereby. The problem of the processing of proteins and polysaccharides as the principal macromolecular components of food belongs to the field of the physical chemistry of polymer solutions; it also has a direct bearing on the modelling of multicomponent biopolymer systems and in addition on the synthesis and employment of polymers for medical purposes.

The questions associated with the conversion of protein into various forms of food can be divided into two groups: (1) structure formation in proteins mixed with other foods in order to obtain food products with a specified structure and physicochemical properties; (2) the imparting of the necessary colour, flavour, and smell to the products with the aid of food dyes and flavouring and aromatic agents and also their enrichment in aminoacids, vitamins, and other essential dietary factors.

This subdivision is, however, arbitrary because the flavour, colour, and smell of a product are associated with its structure and physicochemical properties. Thus the perception of taste arising when food is eaten depends on its mechanical properties, swelling, syneresis, wetting, etc. The vapour pressure of aromatic substances over a food product is determined to a large extent by the sorption of the substances in the bulk of the lipid and aqueous phases, including solubilisation by proteins, and also on the internal and external interfaces. It is natural that the introduction of various additional components into the product can induce the desorption of aromatic, flavouring, and dyeing agents and can alter the structure and physicochemical properties of the product.

In this review only problems concerning the first group, i.e. the physicochemical aspect of the conversion of the protein into NFF will be examined. These questions are analysed from the standpoint of the general physicochemical approach to the problem of the processing of protein developed during recent years. The development of this approach was based on two self-evident considerations. Firstly, food products are multicomponent systems and, secondly, in most cases they are solids and at the same time contain a large amount of water (more than 50%). This is a combination of composition and properties characteristic of gels. In other words, the majority of solid food products can be regarded as gels of proteins and other foods from the physicochemical standpoint. Hence it follows that the principal task faced by investigators is to obtain gels with the necessary composition, structure, and physicochemical properties.[1]

However, it appeared necessary to supplement this general physicochemical task by two others. It is natural to wish to convert any one kind of protein into a wide assortment of food products, which necessitates the preparation of liquid and gel-forming systems with a wide variety of properties. Hence follows the task of regulating the solubility of a protein, its ability to stabilise disperse systems, its ability to form gels, etc. This complex set of physicochemical characteristics, determining the structural functions of protein in non-processed systems, is designated by the concept "functional properties of the protein".[2,3]

The converse problem, namely the preparation of a given dietary product from different proteins, is also important. The fundamental physicochemical phenomena and characteristics common to all proteins are therefore of greatest interest. Processes based on phenomena of this kind should apparently be distinguished by their simplicity, should be susceptible to technological treatment, and should be "universal with respect to the protein".

This review discusses three fundamental physicochemical phenomena underlying the modern methods for converting protein into NFF: the formation of gels from proteins, polysaccharides, and their mixtures, the formation of complexes of proteins and anionic polysaccharides, and the limited thermodynamic compatibility in solution of proteins and polysaccharides and also of proteins with one another. The applied aspects of the problem are only briefly considered in this review. They are discussed in greater detail in a monograph.[1]

II. THE FORMATION OF GELS FROM PROTEINS AND POLYSACCHARIDES

The main physicochemical task arising in the manufacture of NFF consists in the development of methods for the preparation of gels (single-phase and two-phase) with a specified and controllable composition, structure, and mechanical and other physicochemical properties.

The problem of the preparation of NFF is to some extent close in its character to other physicochemical problems arising in the manufacture of polymer articles via a solution—in particular in the processing of technical polymers.[4,5] This analogy is, however, by no means complete. In the first place the fundamental multicomponent nature of the processed food systems and of the final products, together with the wide variety of the functions performed by individual components, is responsible for the complexity and the multiplicity of aspects of the physicochemical problems associated with the regulation of the composition and properties of the products, which is not usually characteristic of technical polymers. The second important feature of food systems, which distinguishes them from technical polymers, is that in the former case the gel state is characteristic not only of the intermediates but also of the final products. Accordingly, there arises a complex set of requirements which must be met by the physicochemical properties of the finished food products as gels. These properties determine in their turn the food value and the organoleptic and technological characteristics of the products.[6]

Three types of processes for the conversion of liquid solutions of biopolymers into the gel state are used in the preparation of NFF: thermotropic, ionotropic, and lyotropic gel formation. In the first case the change in the temperature of the solution plays the main role, in the second case it is the change in the ionic composition of the system, and in the third the change in the concentration of the biopolymer. The last type of gel formation constitutes the basis of the technology of the manufacture of protein products with a porous structure, but the nature of the processes occurring under these conditions has been very little studied.[6]

An example of ionotropic gel formation is the preparation of calcium alginate and pectinate gels. The technology of the manufacture of pasta, cereals, and potato products is based on these processes.[7-12] In the preparation of three-dimensional food products based on calcium alginate and pectinate gels, the main difficulty consists in ensuring the homogeneity of their structure, because the high rate of the interaction of calcium ions with the molecules of polyuronides precludes a satisfactory mixing of the reactants. The known methods for the preparation of isotropic calcium alginate and pectinate gels are apparently based on the regulation of the activity of calcium ions in the reaction system.

The ionotropic gel formation process has found a wider application in the preparation of one- and two-dimensional gels, i.e. fibres and films.[13,14] The diffusion of precipitant ions into solutions of polyuronides is used in such cases. Gels with a well developed phase structure, reproducing the structure of many biological tissues, are obtained in this way.[1,15-18] Among the methods for the ionotropic fibre formation, the matrix spinning process has been studied systematically. This procedure makes it possible to process proteins regardless of their spinnability and to regulate the functional properties of the fibres within wide limits.[19-21] The calcium ion-stabilised interfacial absorption layers containing proteins and polyuronides ensure an exceptionally high resistance of emulsified food products to coalescence.[22]

A method whereby the boundary conditions for ionotropic gel formation can be characterised has been developed.[23] It consists in the determination of the minimum concentrations of reactants sufficient to fix the shape of a drop of the polyelectrolyte solution introduced into a solution of a polyvalent metal salt. Fig.1 illustrates gel–liquid solution diagrams for sodium alginate–polyvalent metal chloride systems. At comparatively low concentrations of the cross-linking agent, namely the polyvalent metal ion, the boundary gel formation conditions are determined by the ion-exchange equilibrium constant. With increase in the concentration of the cross-linking agent, conditions are reached under which the boundary concentration of the polyelectrolyte ceases to depend on the concentration of the polyvalent metal ion. This polymer concentration has been called the "critical gel formation concentration". It apparently depends on the molecular weight and the conformation of the macromolecules. The method indicated is particularly convenient for the determination of the conditions for the formation of gels from anionic polysaccharides in the presence of proteins,[22] which is important in the solution of many applied problems, for example, in the conversion of the polysaccharide phase of a two-phase liquid protein–polysaccharide–water system into the gel state (see below).

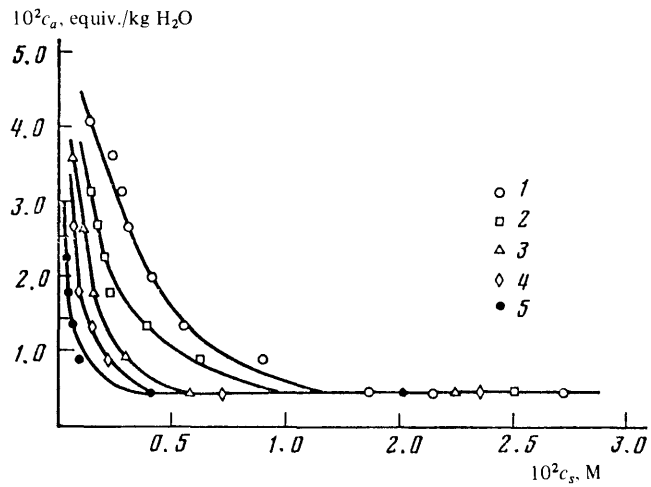

Figure 1. The boundary conditions for gel formation in the sodium alginate–polyvalent metal chloride systems;[22] c_a = concentration of sodium alginate; c_s = concentration of polyvalent metal chloride: *1*) $CaCl_2$; *2*) $SrCl_2$; *3*) $BaCl_2$; *4*) $CuCl_2$; *5*) $LaCl_3$.

Thermotropic gel formation has been investigated in relation to soya bean globulins (SBG), ovalbumin, and also gelatin and many polysaccharides. The thermotropic gel formation from solutions of proteins and polysaccharides has also been investigated, which constitutes the next step in the modelling of multicomponent food systems.[6]

1. The Thermotropic Formation of Gels from Globular Proteins

Thermotropic gel formation is a consequence of the thermal denaturation of globular proteins.[24-28] The study of the thermal denaturation of SBG in a dilute solution by the

method of precision scanning calorimetry[29] showed that the 7*S*-component of the globulin fraction denatures at lower temperatures than the 11*S*-component (Fig.2).[30] The temperature and enthalpy of the denaturation of the principal SBG components increase linearly with increased NaCl concentration. The slope of this relation (for the denaturation temperature), which is equal to the lyotropic constant K_S, is unusually high—about 20 K mol^{-1} litre^{-1}. The ratio of the lyotropic constant to the denaturation temperature, which characterises the magnitude of the lyotropic effect, increases linearly with increasing mole fraction of the hydrophobic units in the protein molecule. The unusually strong influence of NaCl on the denaturation temperature of the principal SBG components can be explained by the comparatively high content of hydrophobic units and their complete masking in the native state. The differences between the enthalpies and entropies of transport of the denatured and native forms of the principal SBG components from water to an NaCl solution are positive and also increase linearly with increasing salt concentration. This shows that the influence of the salt on the thermal denaturation of SBG is based on the decreased degree of hydration of the protein.

The influence of the gel formation conditions on the structure of thermotropic SBG gels has been investigated by the stress relaxation and electron microscopic methods.[31,32] It has been established with the aid of the multifactorial extreme experimental design method that the variation of the modulus of shear of the above gels as a function of temperature and the duration of heating has a single maximum and that its position (95° ± 5 °C; 35 ° 5 min) is independent of the protein concentration. At the same time the relaxation properties of SBG gels depend exclusively on the heat treatment temperature. The explanation is that the temperature (but not the duration) of the heat treatment determines the composition of the SBG components involved in the gel formation process.

The relaxation properties of thermotropic SBG gels can be characterised unambiguously by the parameter $\bar{H} = -[\partial F(\tau)/\partial \ln(\tau)]$, where $F(\tau)$ is the normalised relaxation function, representing the ratio of the relaxation moduli at a certain time τ and at $\tau_0 = 1$ min. In the range from 70° to 115 °C the dependence of the parameter $\bar{H}$ on the heat treatment temperature is linear (Fig.2). According to scanning calorimetric data, the content of the denatured forms of the 11*S*-globulin increases monotonically with increase in temperature over this range and hence also the degree of its involvement in the gel formation process. The deviation of the $\bar{H} = f(T)$ relation from linearity above 115 °C is apparently induced by the increasing contribution of degradative processes.

Experimental data on the isothermal stress relaxation in SBG gels at different concentrations have been generalised in the form of a concentration-invariant relaxation curve as a result of its reduction with respect to the modulus but without its reduction with respect to time.[33] Analogous results have been obtained also in the study of the rheological properties of thermotropic ovalbumin gels and also the gels of a number of anionic polysaccharides.[34] The absence of reduction with respect to time shows that the rate of relaxation processes in gels is independent of the polymer concentration, which is a characteristic of a microheterogeneous gel structure, in many respects similar to that of micellar surfactant solutions. An increase of the polymer concentration in a solution with a microheterogeneous structure leads to an increase in the number of structural elements—associated macromolecular species, without altering the composition and structure of such species. The latter factor determines the concentration invariance of the rate of relaxation processes as well as other intensive properties of the solution. Thus a study[35] of the concentration dependence of the relative activity coefficient of counterions† in solutions of anionic polysaccharides showed that, after the tentative transition to the region of semidilute solutions, this quantity becomes constant.

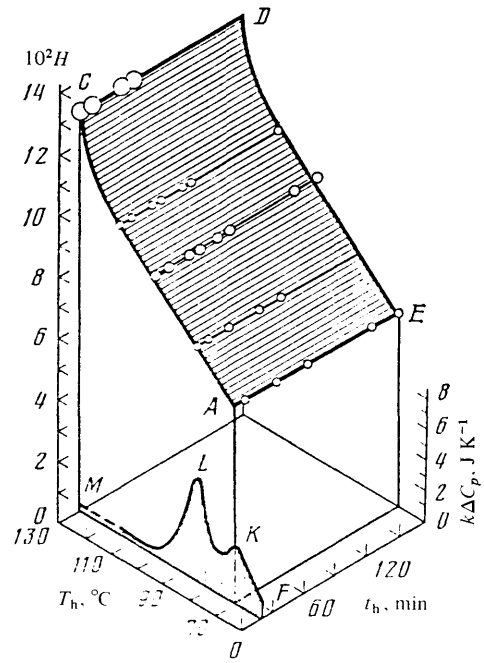

Figure 2. Dependence of the slope of the normalised relaxation function for the thermotropic gels of the globulin fraction of soya beans at 25 °C ($\bar{H}$) (left-hand ordinate axis) on the temperature and duration of the heat treatment in the gel formation process (the *ACDE* surface). Thermogram for a solution of the globulin fraction is plotted on the facing plane (the right-hand ordinate axis; k = scaling factor, the value of which is unimportant) obtained at a scanning rate of 2 K min^{-1} (the *FKLM* curve).[30]

The parameters for the reduction of the relaxation curves with respect to the modulus is proportional to the equilibrium modulus of elasticity. Operating with this parameter, it is possible to determine the scaling relations for the equilibrium modulus of elasticity despite the fact that this modulus cannot be measured for the majority of the protein and polysaccharide gels investigated owing to the low rate of the relaxation process. The concentration dependence of the equilibrium modulus of elasticity of SBG,[33] ovalbumin, as well as a gelatin and agar[36] gels is described by the theoretical Hermans relation[37] derived for a model of the gel formation process as a random reversible association of linear

† The relative activity coefficient of an ion is the ratio of its activity coefficient in the test solution to its activity coefficient in the solution of its chloride at the same equivalent concentration.

identical macromolecules without cyclisation and with formation of network nodes via a bimolecular mechanism.

Hydrophobic interactions play a leading role in the thermotropic formation of gels from SBG. Thus thermotropic SBG gels are soluble in 8 M urea solution, but are insoluble in 0.01 M solution of β-mercaptoethanol, a substance which ruptures disulphide linkages. Under the influence of urea, thermotropic SBG gels and native proteins decompose into virtually identical subunits or their dimers. On the basis of ^{1}H NMR data, it has been suggested that the packing densities of the polypeptide chains in the structural elements of gels and in the subunits of native proteins are comparable. In the 17.5% gel, one structural element consists of ~20 subunits.

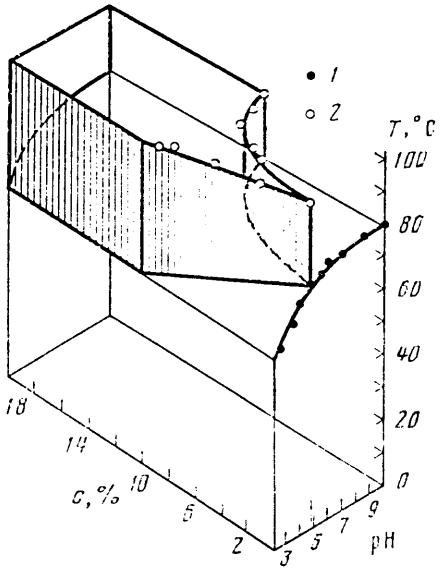

Figure 3. The phase diagram for the ovalbumin–water system at different temperatures, pH, and protein concentrations [*1*) pH dependence of the denaturation temperature; *2*) pH dependence of the gel formation threshold]; the region of the gel state is shown shaded and the isoelectric point is indicated by an arrow.

Taking into account the decisive importance of hydrophobic interactions in the formation of SBG gels, one can assume that the gel-forming capacity of these proteins is correlated with the Tanford–Bigelow hydrophobic parameter, which is defined as the average free energy for the transfer of a polypeptide chain unit from the hydrophobic interior of the protein macromolecule to an aqueous environment.[38,39] According to this criterion, the gel-forming capacity of the monomeric forms of the basic soya bean globulins should decrease in the sequence 2,8*S*-globulin > *B* > β > α > *A*, where *A* and *B* are respectively the acid and basic subunits of 11*S*-globulin and α and β are the heavy and light subunits of the 7*S*-globulin. Analysis of the sol fraction showed that the acid subunits of the 11*S*-globulin do indeed have the lowest gel forming capacity among the monomeric forms of the basic soya bean globulins and accumulate in the sol fraction during gel formation.

According to the results of Maleev and Gasan,[40] the denaturation temperature of ovalbumin gels is almost independent of the ovalbumin concentration in solution. The phase diagram for the ovalbumin–water system is illustrated in Fig.3#. The dependence of the critical gel formation concentration of albumin on the pH passes through a sharp minimum near the isoelectric point (IEP), which means that the rate of gel formation and the functionality of the ovalbumin molecules at the IEP are maximum. It is known[41] that the negative contribution of the charge fluctuations to the chemical potential of the protein in solution is significant precisely at the IEP.

As in the case of SBG gels, the dependence of the modulus of elasticity of the ovalbumin gels on the temperature and the duration of heat treatment has a single maximum§. The optimum gel formation time (30 min) is independent of pH, but the optimum temperature, which is 80 °C under conditions remote from the IEP, increases sharply in the pH range 4.0–5.5. Gels formed under conditions remote from the IEP consist of a single phase, while those produced in the vicinity of the IEP consist of two phases. Each of these groups is characterised by its own mechanical relaxation function. Since the temperature and duration of the heat treatment of the solution, the pH, and the protein concentration (*c*) influence only the equilibrium modulus of elasticity, all the relaxation curves obtained can be described by two normalised relaxation functions corresponding respectively to single-phase and two-phase gels.

The form of the generalised relaxation curve for ovalbumin gels¶ (Fig.4) makes it possible to assign these gels to the systems at the beginning of the zone corresponding to the transition from the vitreous to the highly elastic state.[42] The mechanical relaxation curves for the gelatin,[43] maltodextrin,[44] and a number of anionic polysaccharide[45–48] gels have an analogous character. The form of the relaxation curves shows that the relaxation processes localised in the associated macromolecular species making up the three-dimensional network are retarded.[34] On the other hand, during a time interval corresponding to about seven decadic orders of magnitude, the temperature-invariant relaxation curve for the SBG gel[33] has the form characteristic of amorphous cross-linked polymers at the end of the transition zone or at the beginning of the zone corresponding to the plateau.[42]

2. The Thermotropic Formation of Gels from Polysaccharides

In constrast to the formation of globular protein gels, the processes involving the thermotropic formation of polysaccharide gels are in most cases reversible. By virtue of the relative simplicity of the chemical structure of polysaccharides, an inter-relation between the chemical structure

#N.V.Grinberg, T.M.Bikbov, V.Ya.Grinberg, T.S.Chaika, I.A.Vaintraub, and V.B.Tolstoguzov, Int.J.Biol.Marcomol., 1985, 7, 152.

§N.V.Grinberg, T.M.Bikbov, V.Ya.Grinberg, and V.B.Tolstoguzov, Colloid and Polymer Sci., 1985, 33 (In the press).

¶V.Ya.Grinberg, N.V.Grinberg, T.M.Bikbov, and V.B.Tolstoguzov, "Materialy V Vsesoyuznogo Soveshchaniya 'Protsessy Studneobrazovaniya v Rastvorakh Polimerov'" (Proceedings of the Vth All-Union Conference on 'The Gel Formation Processes in Polymer Solutions'), 1985, Part 1, p.96.

of biopolymers of this class, their conformation, and their gel-forming capacity can be traced.[49-51] Like other thermotropic gels, particularly gelatin gels, the thermotropic polysaccharide gels are formed when the quality of the solvent is impaired. Gel formation must be preceded by a stage in which macromolecular associated species are formed and the gel is produced as a result of the combination of these species in a three-dimensional network.[52] Certain features of the relaxation behaviour of the polysaccharide gels, which follow from the gel formation mechanism described, are discussed in the previous Section.

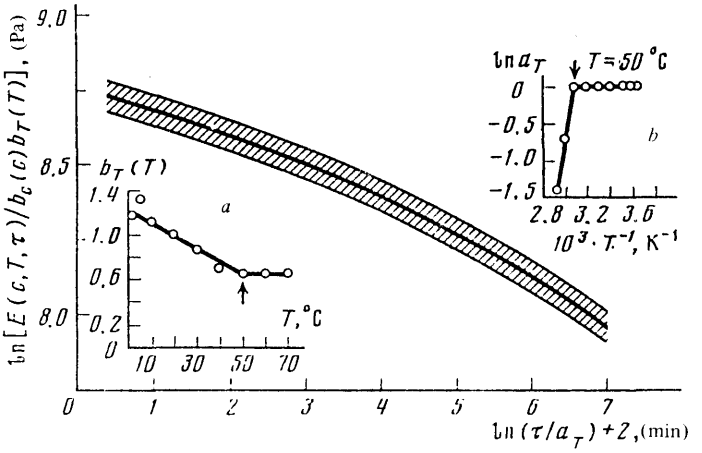

Figure 4. $c-T$ invariant generalised relaxation curve for single-phase thermotropic ovalbumin gels reduced to the state with c_0 = 10% and T_0 = 50 °C [E = relaxation modulus, c = protein concentration, T = temperature, τ = time, $b_c(c) = E(c, T, \tau)/E(c_0, T, \tau)$, and $b_T(T) = E(c, T, \tau)/E(c, T_0, \tau)$ are the parameters of the reduction of the modulus with respect to the concentration and temperature, and a_T = parameter of the reduction of time with respect to temperature]; the half-width of the shaded band is equal to the standard deviation of the experimental points from the average curve; the temperature variations of the parameters of the reduction of the modulus and time with respect to temperature are shown in the inserts *a* and *b*.

The thermotropic formation of pectin gels takes place at pH 4 in the presence of substances which reduce the activity coefficient of water (sucrose, glycerol, etc).[55] The gel-forming capacity of pectins depends critically on the degree of their esterification (DE). This dependence is determined by at least two factors: (1) the influence of the DE on the flexibility of the pectin chain, which is responsible for the possibility of the appearance of the optimum number of contact zones in gel formation; (2) the influence of the DE on the free energy of the intermolecular interactions in the contact zones. Apparently the first factor is of decisive importance, since the maximum strength and moduli or elasticity of the gels are attained for DE ≅ 50%,[56,57] i.e. when the flexibility of the pectin chain is a maximum.[35,58] The rate of gel formation for this DE is a minimum.[56] Spectroturbidimetric study of the structure of the gels showed# that, under these conditions, systems with minimum dimensions of the structural elements, which corresponds to the maximum strength of the gel, are formed (Fig.5).

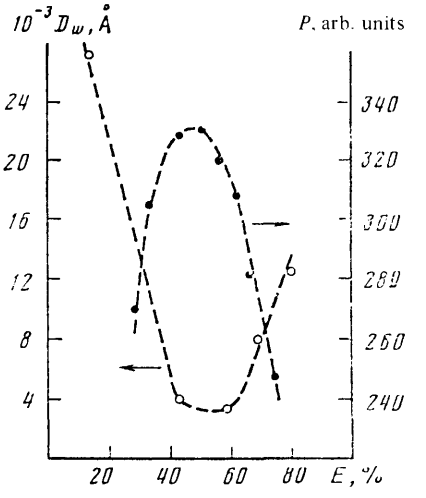

Figure 5. Dependence of the effective diameter of the structural elements (D_w) and of the stability (P)[57] of pectin gels on the degree of esterification (E) of pectin; pectin concentration 1%; pH 2.2; solvent—1:1 water–glycerol mixture.

The study of the time variation of the structure and properties of gels has shown that there exist two types of networks: the thermodynamically stable and metastable networks. The latter type includes the maltodextrin[44] and methylcellulose hydrogels†. On prolonged storage, these gels pass into a past-like state, which is manifested, in particular, by a decrease of the heat of fusion of maltodextrin gels. According to electron microscopic data,[44] the structural elements of the maltodextrin gel network rearrange after a time and form isodiametric associated species. The opposite direction of the structure-forming process has been observed for gelatin gels.[53] The stability of such gels increases with time.[54] The moduli of elasticity of pectin[45] and other anionic polysaccharide gels vary analogously. For these polymer–solvent systems, the gel state is thermodynamically stable.

†E.V.Grishchenkova, E.E.Braudo, and V.V.Tolstoguzov, Colloid and Polymer Sci., 1985, **263** (in the press).

The standard enthalpy of decomposition of the pectin gel network nodes in mixtures of water with sucrose[45] and glycerol[48] is 7–39 kJ mol^{-1}. Such low enthalpies are characteristic of solutions of semirigid-chain polymers incapable of conformational transformations under gel formation conditions. The formation of network nodes in such systems is not accompanied by appreciable losses of conformational entropy. The gel formation process therefore becomes thermodynamically favourable even for a small decrease of enthalpy. This type of gel formation has been called non-cooperative.[34]

An analogous picture has been observed for maltodextrin gels. For a 20% gel, the decomposition of the network nodes is characterised by the following thermodynamic

#I.G.Plashchina, Abstract of Candidate's Thesis in Chemical Sciences, Institute of Organoelemental Compounds, USSR Academy of Sciences, Moscow, 1984.

parameters: $\Delta H^0 = 25$ kJ mol^{-1},[34,44] $\Delta S^0_{25\,^\circ C} \cong 32$ J mol^{-1} K^{-1}; $\Delta G^0_{25\,^\circ C} \cong 15$ kJ mol^{-1}.

The formation of gels from gelatin proceeds quite differently. The standard enthalpy of decomposition of the network nodes of a 5% gel is 300 kJ mol^{-1}.[34,43] In this case (the cooperative mechanism of gel formation) the appearance of network nodes is accompanied by the formation of helices from the flexible macromolecules capable of conformational transformations. The high enthalpy of the gel formation process compensates for the large losses of conformational entropy.

Among the anionic polysaccharides investigated, the galactans converted into the sulphate form, namely κ-carrageenan and furcellaran, are conformationally labile. On cooling their solutions to room temperature, both polysaccharides undergo the coil–helix conformational transformation.[49] The formation of these polysaccharide gels is promoted by certain metal ions, including potassium ions.

In the existing theories the formation of helices from κ-carrageenan macromolecules is regarded as the primary process in gel formation,[59-61] as happens in the formation of gelatin gels.[62] The function of the metal ions promoting the formation of the κ-carrageenan gel reduces to promoting helix formation[63] and to participation in the formation of contacts between the helical sections of the macromolecules. However, it has been shown that the κ-carrageenan macromolecular associated species and gel network are formed under the influence of potassium ions above the temperature range of the coil–helix conformational transition. Thus the effective size of the κ-carrageenan macromolecular associated species does not change in the conformational transition.[64]

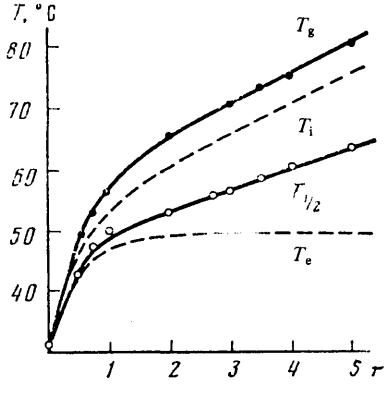

Figure 6. Dependence of the gel formation temperature (T_g) and the temperature of the onset (T_i), middle ($T_{1/2}$), and end (T_e) of the coil–helix transition of a 1.5% solution of κ-carrageenan on the KCl concentration; r = ratio of the equivalent concentrations of KCl and κ-carrageenan.

According to Plashchina et al,[46] the melting point of the 1.5% κ-carrageenan gel exceeds the temperature of its complete conversion into the helical form by 13°. Fig.6 illustrates the dependence on the KCl concentration of the gel formation temperature of the 1.5% κ-carrageenan solution and also the temperature of the onset, the middle, and the end of the coil–helix transition in this solution§. Evidently, at [KCl] > 3.7×10^{-2} M, the gel formation temperature is above the helix formation temperature range. It has been suggested that the κ-carrageenan gel network is formed as a result of the cross-linking of the polysaccharide macromolecules by the potassium ions, forming coordinate bonds with the hydroxy-groups. An essential condition in the formation of the gel network is the neutralisation of the charge of the sulphate groups by the potassium ions.

The conformational state and the stability of the conformations of the macromolecules determine the thermorheological behaviour of the κ-carrageenan gels§. Fig.7 illustrates the temperature dependence of the highest Newtonian viscosity of the 1.5% gel in terms of the variables of the De Guzman–Arrhenius equation. It is seen that the experimental temperature range can be divided into three regions:

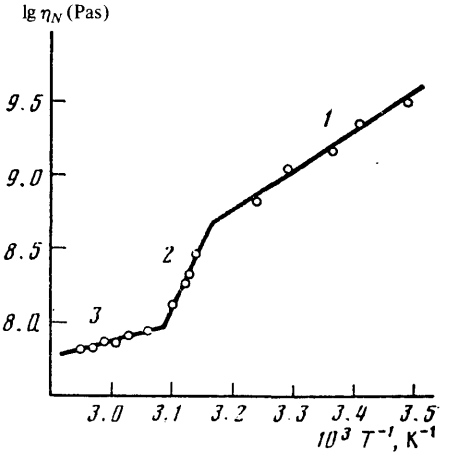

Figure 7. Temperature dependence of the maximum Newtonian viscosity (η_N) 1.5% κ-carrageenan gel.

(1) t < 41 °C—the temperature range in which the helical conformation of the macromolecules is stable (ΔH^0 = 36 kJ mol^{-1}, $\Delta S^0_{25\,^\circ C} \cong 135$ J mol^{-1} K^{-1}; $\Delta G^0_{25\,^\circ C} \cong -4$ kJ mol^{-1} [34]);

(2) 41 °C ≤ t < 52 °C—the region of the helix–coil conformational transition ($\Delta H^0 = 235$ kJ mol^{-1}; $\Delta S^0_{41\,^\circ C} \cong 775$ J mol^{-1} K^{-1}; $\Delta G^0_{41\,^\circ C} \cong -9$ kJ mol^{-1} [34]);

(3) 52 °C ≤ t ≤ 66 °C—the temperature range in which the κ-carrageenan gel network is formed by macromolecules which have lost their helical structure ($\Delta H^0 = 11$ kJ mol^{-1}).

It is seen from the thermodynamic parameters presented that in region 2 the character of the gel formation is cooperative. In regions 1 and 3 the gel formation is non-cooperative: in the former case this can be accounted for by the stability of the helical conformation, as a result of which the polysaccharide assumes the properties of a semirigid-chain polymer, while in the latter case it can be explained by the impossibility of the appearance of the helical conformation.

Apparently the higher stability of the helical conformation of furcellaran, due to the lower content of sulphate groups compared with κ-carrageenan, is responsible for the non-cooperative character of the formation of this polysaccharide gel in a mixture of sucrose (70%) and water up to 50 °C ($\Delta H^0 = 19$ kJ mol^{-1}).[34,47]

§I.G.Plashchina, I.R.Muratalieva, E.E.Braudo, and V.B.Tolstoguzov, Carbohydr.Polymers, 1985, 5 (in the press)

Thus non-cooperative gel formation is largely characteristic of the polysaccharides investigated. It has been observed for a polysaccharide with a highly rigid chain (pectin), for polysaccharides with a helical conformation stable under the experimental conditions (maltodextrin, furcellaran, and κ-carrageenan below 41 °C), and also in gel formation above the temperature range of the helix–coil transition (κ-carrageenan above 52 °C).

3. The Formation and Properties of Thermotropic Gels Containing Proteins and Polysaccharides

The following types of multicomponent gels have been differentiated:[1,65,66]

(1) Filled gels in which one of the macromolecular components functions as the gel-forming agent, while the others play the role of fillers. Gels filled with particles of a disperse phase can also be included in this group.

(2) Mixed gels in which there are two or more networks formed by different gel-forming agents. The necessary conditions for the formation of mixed gels are thermodynamic compatibility of the gel-forming agents in solution and the absence of a specific interaction between them.

(3) Complex salts whose three-dimensional network is formed by the products of the interaction of different macromolecular components.

The properties of the mixed and complex gelatin and calcium and sodium alginate and pectinate gels have been summarised in a review[66] and in a monograph.[1]

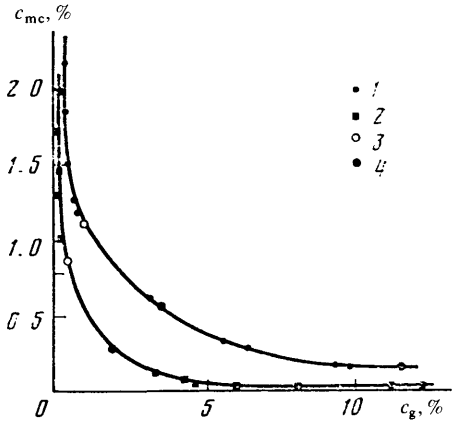

Figure 8. The phase diagram of the gelatin–methylcellulose–water system at 35 °C;[67] c_{mc} and c_g are the concentrations of methyl cellulose and gelatin: 1) binodal curve at pH 3.0; 2) binodal curve at pH 4.75 (isoionic point of gelatin); 3) threshold point; 4) critical point.

The formation of mixed and single-phase unfilled gel is limited by the low compatibility of the macromolecular components in the absence of complex formation between them. Fig.8 presents the phase diagram for the gelatin–methylcellulose–water system at 35 °C (at this temperature none of the components form a gel).[67] It is seen from the figure that the compatibility of gelatin with methylcellulose increases somewhat as the pH of the system shifts from the isoelectric point of gelatin. This can be explained by the suppression of the self-association of gelatin induced by the Coulombic interaction due to charge fluctuations as a consequence of the increasing electrostatic repulsion.[68] The introduction of NaCl does not lead to an appreciable increase of compatibility, since the decrease in the degree of self-association of gelatin is compensated by the increase in the degree of self-association of methylcellulose under the influence of NaCl. The asymmetry of the gelatin–methylcellulose–water phase diagram, which is characteristic of quasi-binary protein–polysaccharide systems, is striking.[69]

In the absence of complex formation, an enhancement of structure formation in individual components of single-phase multicomponent gels, i.e. the development of intramolecular and intermolecular contacts between the macromolecules of one component at the expense of the polymer–solvent contacts, is observed. This phenomenon is due to the excluded volume effect.[6,70,71]

An important example of a process determined by the development of intramolecular polymer–polymer contacts is provided by the coil–helix transition. Fig.9 illustrates the influece of dextran on the mutarotation of gelatin in solution at 6 °C. It is seen that the presence of only 0.2% of dextran, which is 5% of the concentration of gelatin, induces a sharp acceleration of the conformational transition of the latter. There is a simultaneous increase of the rate of gel formation. The coil–helix transition leads to the expansion of the region of incompatibility of gelatin and dextran.[72]

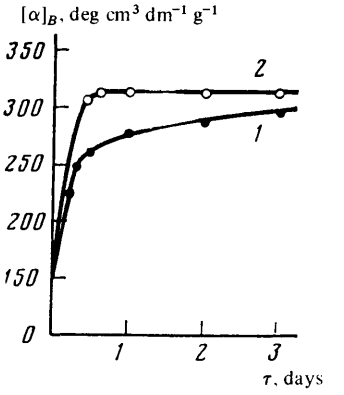

Figure 9. The influence of dextran on the mutarotation of a 4% gelatin solution;[72] $[\alpha]_B$ = specific optical rotation at λ = 436 nm: 1) water; 2) 0.2% dextran solution.

The enhancement of structure formation in the components of a mixed gel is manifested also by a decrease of the critical gel formation concentration¶. Fig.10 shows that a mixed gel of gelatin and agarose is formed at concentrations of the polymeric components such that each separately is still incapable of forming a gel network. An analogous phenomenon has been noted for mixed thermotropic agar and bovine serum albumin gels.[73]

The study of the viscoelastic properties of gelatin gels containing globular proteins or a polysaccharide (dextran) showed that the presence of fillers affects the effective

¶A.M.Gotlieb, I.G.Plashchina, E.E.Braudo, and V.B.Tolstoguzov, Colloid Polymer Sci., 1985, 263 (in the press).

number of gel network nodes (the equilibrium modulus of elasticity), while the rate of relaxation processes remains unaltered in most cases.[72,74]

The properties of multicomponent gels naturally depend on their phase state. In certain cases extrema appear on the gel property–composition curves, which may be attributed to a transition from the single-phase to the two-phase state. Such a transition in the region of the filler concentration corresponding to the minimum pliability (the maximum modulus of elasticity) has been established for the gelatin–dextran–water system by electron microscopy.[72] The decrease of pliability in the single-phase state can be accounted for by the increase of the effective number of gelatin gel network nodes under the influence of the filler (dextran) by virtue of the excluded volume effect. In the two-phase state the drops of the phase enriched in dextran form defects in the gelatin gel network.

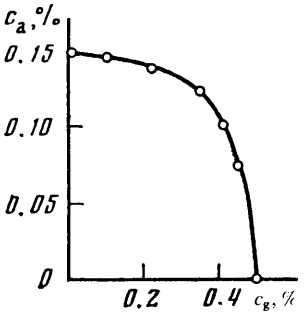

Figure 10. Dependence of the critical concentration for gel formation on the composition of the gelatin–agarose–water mixture at 8 °C; c_g = gelatin concentration; c_a = agarose concentration.

It has been suggested that in the general case the region of filler concentrations corresponding to the onset of the increase in the pliability and in the degree of swelling of gels be called the limit of the structural compatibility of the filler and the gel matrix.[6] This limit depends both on the nature of the matrix and on the molecular characteristics of the filler.[74,75] The character of the influence of the molecular weight of dextran on the limits of its structural (thermodynamic) compatibility with the gelatin gel matrix can be seen from Fig.11.[72]

In the region of the two-phase state each of the polymeric components is concentrated in one of the phases. In this case the properties of the mixed gels are determined primarily by those of the continuous phase. When the composition of this system is varied within wide limits, phase inversion, accompanied by a change in the properties of the gel, takes place.[6,36,75,76]

III. COMPLEX FORMATION IN SOLUTIONS OF PROTEINS AND ANIONIC POLYSACCHARIDES

The interaction between proteins and anionic polysaccharides has been studied by many workers and certain aspects of this phenomenon have been surveyed in a number of reviews.[77–81] The first systematic studies, which were devoted mainly to the nature of the phase separation in solutions of proteins and anionic polysaccharides (i.e. to the formation of complex coacervates or insoluble complexes), showed that the protein–polysaccharide complexes (PPC) are stabilised mainly by electrostatic forces. On the other hand, the complex formation between anionic polysaccharides and proteins, demonstrated in a number of studies at a pH above the isoelectric point of the protein (where the macroreactants bear like charges),[82–86] as well as the complex formation between neutral polysaccharides and proteins (not lectins),[87,88] indicate a significant role of the secondary non-electrostatic interactions in the stabilisation of protein–anionic polysaccharide complexes.

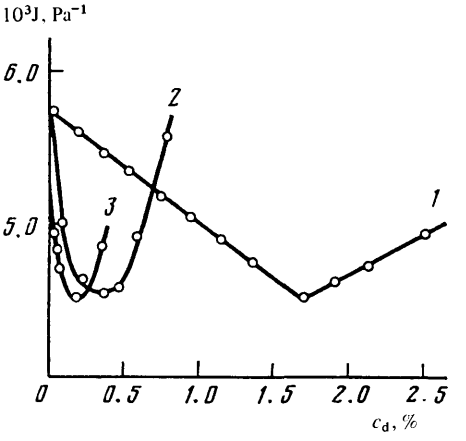

Figure 11. The influence of the dextran concentration (c_d) on the pliability J of 10% gelatin gels;[72] molecular weight of dextran: *1*) 20 kD; *2*) 65 kD; *3*) 500 kD.

The functional properties of the PPC, such as solubility, surface activity, and rheological characteristics, differ significantly from the analogous properties of the initial macroreactants and, what is especially important, can be regulated within wide limits.

Water-soluble PPC are of interest for the food technology, but their structures and properties have been little studied. The investigation of the equilibrium nature of the PPC, the nature of the forces stabilising them, the molecular structure of the PPC and the bound protein, and the functional properties of the complexes is urgently required.

1. The Non-Equilibrium Complexes

Studies of the formation of the PPC have shown that, at sufficiently low pH and ionic strengths, the latter do not correspond to equilibrium: their properties and in particular their solubilities† depend on the method of preparation.[89] Thus, when solutions of the macroreactants are mixed under the conditions of vigorous complex formation (at a pH below the IEP), "mixing complexes" (M-complexes), which are sparingly soluble in water, are formed. On the other hand,

† The terms "soluble" and "insoluble" which we use in relation to the non-equilibrium complexes are arbitrary, since strictly speaking they should refer to a stable thermodynamic equilibrium.

on slow titration of the solution, when conditions in the medium change in such a way that the interaction gradually intensifies, readily soluble "titration complexes" (T-complexes) are produced.

The difference between the solubilities of the M- and T-complexes are clearly manifested in nephelometric titration (Fig.12). The turbidity of the system serves in this instance as a semiquantitative characteristic of the yield of the insoluble PPC.

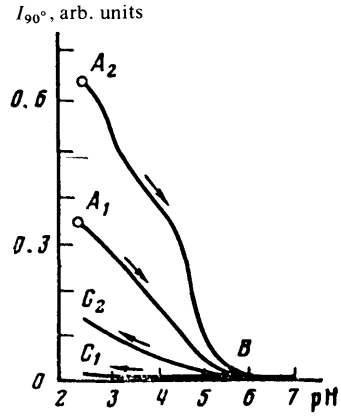

Figure 12. Nephelometric titration curves for solutions of complexes of bovine serum albumin and dextran sulphate in proportions, by weight, of 1:1 and 2.3:1 (the A_1BC_1 and A_2BC_2 curves); overall concentration of macroreactants 0.1 g litre^{-1}.

The differences between the solubilities for the M- and T-complexes (aggregation hysteresis) are particularly marked for the PPC of highly sulphated polysaccharides such as dextran sulphate and heparin. Furthermore, a high aggregation stability is characteristic of the solutions and suspensions of these PPC: the light scattering and the wave exponent (sensitive to changes in the size of the scattering particles) can be constant for several days at room and elevated (40–50 °C) temperatures.

The non-equilibrium PPC have been studied in greatest detail in relation to the complexes of the high-molecular-weight dextran sulphate with proteins, in particular with bovine serum albumin (BSA).[90] The character of the interaction of BSA with dextran sulphate varies sharply as a function of the pH. In the range 5.6 $\leqslant$ pH $\leqslant$ 8.5 (the range corresponding to a relatively weak interaction) the properties of the PPC are independent of the method of their preparation, which indicates the equilibrium character of the complex formation. Analysis of the composition of the water-soluble complexes at pH 5.6 showed that the sorption of BSA by dextran sulphate is non-cooperative, i.e. the protein–protein interaction does not have an appreciable influence on the binding of the protein to the polysaccharide. Under these conditions, the PPC are not aggregated: each particle consists of one dextran sulphate molecule.

In the vicinity of the isoelectric point of BSA (5.0 < pH < 5.6) the composition of the soluble complexes is also independent of the way in which they are prepared, but does depend strongly on the pH. At the same time, in the above pH range the aggregation hysteresis is already observed (Fig.12)#.

The fact that in the above pH range a transition is observed from a uniform distribution of the protein molecules between the dextran sulphate chains to a non-uniform distribution is of particular interest. Two discrete fractions of the complex appear in the solution—the rapidly sedimenting α-fraction and the slowly sedimenting β-fraction. Analysis by the method of high-speed sedimentation and gel chromatography showed that the ratio of these fractions varies steadily: with increase of the fraction of BSA in solution, the proportion of the α-fraction rises and that of the β-fraction falls. At the same time the sedimentation coefficients of these fractions also increase. They both consist of a BSA–dextran sulphate complex but differ in composition: the α-fraction is enriched in the protein while the β-fraction is depleted in the latter. The non-uniform distribution of the protein between the polysaccharide chains can be accounted for by the cooperative character of its sorption.[91,92] The transition from the non-cooperative sorption of the BSA to the cooperative sorption is apparently due to the intensification of the interactions between the protein molecules in the PPC species or the decrease of the pH which can be accounted for in its turn by the decrease of the overall charge of the protein, hindering, at a higher pH, the mutual approach of the protein globules.[93,94]

At pH $\leqslant$ 5.0 the sorption of the BSA becomes irreversible. Under these conditions, the α-fraction of the M-complexes of any composition is precipitated. On the other hand, the α-fraction of the T-complexes is readily soluble, provided that the ratio of BSA and dextran sulphate does not exceed 4:1 by weight (critical mixture composition). For a BSA : dextran sulphate ratio of 4:1 and above, the T-complexes are fully precipitated. This ratio also corresponds to the complete disappearance of the β-fraction, which is soluble regardless of the way in which the complexes have been prepared.

The aggregation of the protein–dextran sulphate complexes and the aggregation hysteresis are observed also in concentrated urea solutions. Since the aggregation of proteins in this medium is suppressed, presumably the secondary interactions (hydrogen bonds and hydrophobic interactions) do not play a decisive role in stabilising the aggregates of the protein–dextran sulphate complexes (both equilibrium and non-equilibrium). The formation of non-equilibrium aggregates is apparently due to electrostatic interactions. At the same time the number of ionic bonds between the macroreactants is independent of the way in which the complexes have been obtained, since hysteresis in the sorption of protons is not observed in the potentiometric titration of BSA–dextran sulphate solutions. One can therefore assume that the differences between the M- and T-complexes are caused by the different distributions of the protein molecules between the polysaccharide chains: the T-complexes consist of species with a single dextran sulphate chain (monomatrix complexes), while the M-complexes (the α-fraction) consist of three-dimensional intertwined networks made up of dextran sulphate chains cross-linked by the protein (polymatrix complexes).

Thus mixing of BSA and dextran sulphate solutions at pH < 5.0 (for all the ratios investigated) leads to the appearance of a highly aggregated α-fraction, produced as a result of the cross-linking of the random network of the dextran sulphate chain by the protein, together with the readily soluble β-fraction. In the T-complexes

#V.B.Tolstoguzov, V.Ya.Grinberg, and A.N.Gurov, J.Agric.Food Chem., 1985, 33, 151.

obtained when the complex formation equilibrium is "frozen" at pH ~5.0 with subsequent transition to the same conditions as those for the M-complexes, the α-fraction remains soluble up to the protein : dextran sulphate ratio of 4 : 1 by virtue of the electrostatic repulsion between the species bearing like charges and containing one dextran sulphate chain.

2. The Influence of Temperature on the Structure of the Protein Bound in a Complex with the Polysaccharide

The formation of complexes with anionic polysaccharides makes it possible to prevent the thermal coagulation of the protein,[95] which can evidently be explained by the immobilisation of the protein molecules in the complex, preventing the formation of aggregates on denaturation. For example, the coagulation of the BSA–dextran sulphate complex and the absence of the free protein is not observed up to 100 °C (at pH 5.6). The circular dichroism method makes it possible to observe the denaturation of the bound protein to the same high extent as that of the free protein. However, the denaturation of the bound protein is non-cooperative, in contrast to that of the free protein, and is therefore not accompanied by a thermal absorption peak characteristic of the thermal denaturation of free proteins.

3. The Use of the PPC for the Regulation of the Surface Properties of the Protein

The complexes of proteins with anionic polysaccharides have a number of advantages over the initial proteins by virtue of their surface activity. Thus they can ensure a higher stability of emulsions of the "oil–water" type.[96] Fig.13 presents stability diagrams for model emulsions of n-decane in aqueous solutions of BSA and its complexes with dextran sulphate (the latter shows no surface activity and does not itself stabilise emulsions). It can be seen that, over a wide range of protein concentrations, the stability of the emulsions of n-decane in solutions of the complexes is significantly greater. The differences between the emulsifying properties of the protein and its complexes with dextran sulphate diminish with increasing ionic strength, disappearing completely under conditions where the complexes are decomposed.

An analogous increase of the stability of emulsions when the PPC is used instead of the protein has been observed for casein–carrageenan, casein–pectin, human serum albumin–dextran sulphate, and certain other complexes.

It is important to note that the PPC make it possible to regulate the rheological characteristics of the emulsions within wide limits. In particular, one of the versions of the highly viscous (stuffing-like) emulsions stabilised by protein–anionic polysaccharide complexes has been used in the manufacture of cooked sausages.[97]

The properties of the interfacial adsorption layers formed by the PPC have not so far been investigated. However, presumably the structural organisation of the PPC at the interfaces is similar to that which is obtained in complex gels. The formation of the latter and their properties have been investigated in greatest detail in relation to gels of the gelatin–sodium alginate[98,99] and gelatin–pectin[100] complexes, for which significant differences from gelatin gels have been observed. In contrast to the latter, the gelatin–sodium alginate complexes do not melt in the range 30–40 °C and exhibit only an abrupt increase of pliability while retaining other elastic properties up to 100 °C. It is significant that the gel formation in PPC solutions can be observed under conditions where the individual macroreactants do not form gels. An example is provided by the thermoreversible complex gel of casein and sodium alginate§.

IV. THERMODYNAMIC COMPATIBILITY OF PROTEINS AND POLYSACCHARIDES IN SOLUTION

Multicomponent mixtures of polymers are as a rule of a heterophase type; compatibility is attained only when the mixing is accompanied by the evolution of heat. From the standpoint of the technology of the preparation of new forms of food, the study of the thermodynamic compatibility in solutions of the principal classes of food polymers, namely proteins and polysaccharides, was of great interest.

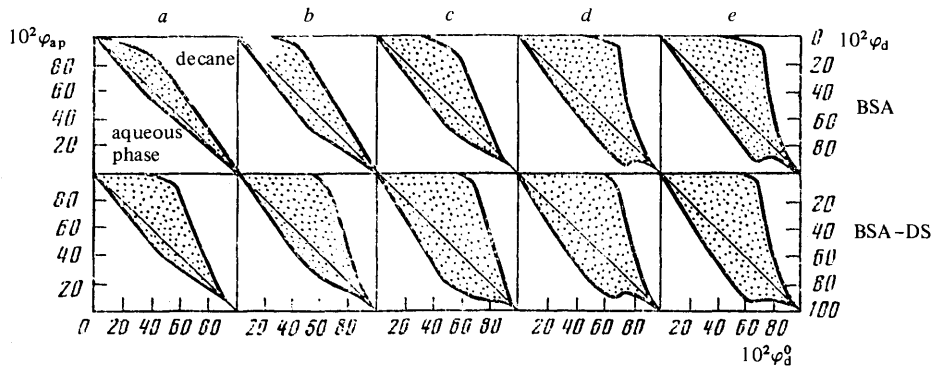

Figure 13. Stability diagrams for n-decane emulsions in aqueous solutions of bovine serum albumin (BSA, upper row) and its complex with dextran sulphate in proportions, by weight, of 1 : 1 (BSA–DS, lower row) at pH 4.0 and an ionic strength of 0.01; ϕ_d^0 = volume fraction of n-decane in the system, ϕ_{ap} = volume fraction of separated aqueous phase, ϕ_d = volume fraction of separated n-decane; BSA concentration (%): *a*) 0.025; *b*) 0.05; *c*) 0.10; d) 0.30; *e*) 0.50.[96]

§M.A.Mukhin, Abstract of Candidate's Thesis in Chemical Sciences, Institute of Organoelemental Compounds, USSR Academy of Sciences, Moscow, 1984.

1. Thermodynamic Compatibility in Protein–Polysaccharide–Water Systems

Although the limited thermodynamic compatibility of gelatin and polysaccharides in solution was observed as early as the end of the previous century[101] and since then has been the subject of a series of studies,[68,102–108] the systematic investigation of thermodynamic compatibility in solutions of polysaccharides and proteins, in the first place globular proteins, was begun only in recent years.

The phenomenology of the limited thermodynamic compatibility in solution has been investigated[68,106,109–114] for the principal classes of proteins and polysaccharides. The fact that the phenomenon of limited thermodynamic compatibility is general has been demonstrated with more than 80 protein–polysaccharide–water systems. All these systems undergo liquid-phase separation with the preferential concentration of the macromolecular components in different phases. This occurs at a fairly high overall concentration of the macromolecular components (usually above 4%) under conditions ensuring the suppression of the association of heterotypical macromolecules and favouring the association of isotypical macromolecules. The principal conditions governing limited thermodynamic compatibility differ for systems containing neutral, carboxylated, and sulphated polysaccharides.

The thermodynamic compatibility of casein[110,111] and the globular fraction of soya beans[112] with different polysaccharides has been studied in greatest detail. Data concerning the influence of the most important thermodynamic variables (pH, ionic strength, temperature, and the molecular weight) on the compatibility of protein and polysaccharides have been obtained. They have been published[110–113] in the form of three-dimensional phase diagrams. As a rule the compatibility diminishes as the pH approaches the isoelectric point of the protein and also with increase of the concentration of the low-molecular-weight salt, temperature, and the molecular weight of the polysaccharide. The sulphated polysaccharides are a known exception. In this case the compatibility increases as the pH approaches the isoelectric point of the protein. The region of total compatibility exists in the vicinity of this point.

The protein–neutral polysaccharide–water and protein–sulphated polysaccharide–water systems have a lower consolute point below a certain concentration of the low-molecular-weight salt. If the salt concentration is below this threshold value, the protein and the polysaccharides indicated are completely compatible. The threshold concentration of the salt depends on its composition and on the pH. The influence of the salt on the thermodynamic compatibility of proteins and neutral polysaccharides is not generally correlated with the positions of the salts in the lyotropic series.

In order to elucidate the nature of thermodynamic compatibility a thermorheological study of the single-phase protein–neutral polysaccharide–water systems has been carried out at different ionic strengths corresponding to the complete or limited compatibility of the macromolecular components at higher concentrations.[114] The excess activation energies for viscous flow, determined by the protein–polysaccharide interaction, were calculated. Positive values of this parameter are characteristic of the conditions ensuring the complete compatibility of the components in the system while negative values are characteristic of systems with limited compatibility, which indicate the predominance of the attraction and repulsion forces respectively between heterotypical macromolecules. Thus it was possible to demonstrate the formation of weak protein–neutral polysaccharide complexes in media with a low ionic strength, where the components are thermodynamically compatible, and their decomposition at a higher ionic strength, i.e. under the conditions of the limited thermodynamic compatibility of proteins and neutral polysaccharides.

2. Thermodynamic Compatibility in Protein–Protein–Water Systems

Data concerning the thermodynamic compatibility of proteins have also appeared recently. It has been shown for nine systems[115] that under certain conditions proteins belonging to different classes in Osborn's classification are compatible only to a limited extent in an aqueous medium. The phase diagrams for certain protein *1*–protein *2*–water systems¶, obtained by the method of the phase volume ratio,[116] are presented in Figs.14 and 15.

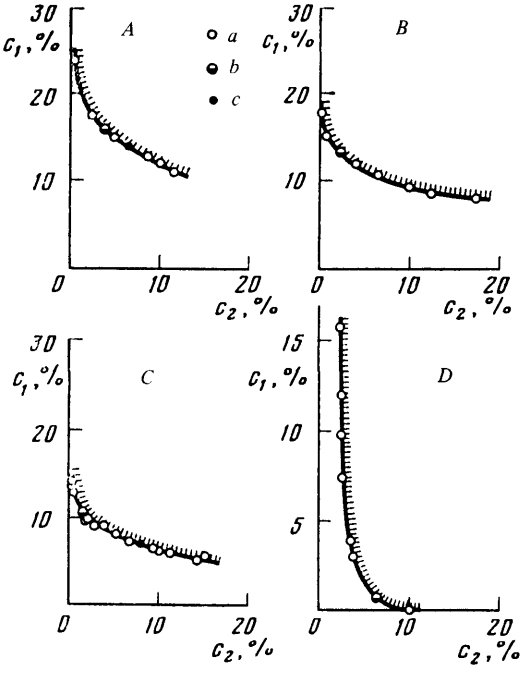

Figure 14. Phase diagrams for certain protein (1)–protein (2)–water systems at 20 °C: *A*) ovalbumin (1)–casein (2)–water (pH 6.6); *B*) ovalbumin (1)–globulin fraction of soya beans (2)–water (pH 6.6); *C*) casein (1)–globulin fraction of soya beans (2)–water (pH 6.9); *D*) casein (1)–gliadin (2)–water (pH 11); c_1 and c_2 are the weight concentrations of proteins (1) and (2) in the system: *a*) points on the binodal curve; *b*) layer separation threshold; *c*) consolute point.

Analysis of the equation of state for polymer *1*–polymer *2*–solvent systems by the Flory–Huggins method leads to characteristics which determine the form of their phase diagrams.[117] In particular, the layer formation threshold, i.e.

¶V.I.Polyakov, O.K.Kireeva, V.Ya.Grinberg, and V.B.Tolstoguzov, Nahrung, 1985, 29, 153.
V.I.Polyakov, I.A.Popello, V.Ya.Grinberg, and V.B.Tolstoguzov, Nahrung, 1985, 29 (in the press).

the point at which the binodal curve is tangential to the straight line making equal intercepts on the coordinate axes, should be displaced towards the axis corresponding to the polymer with the lower molecular weight, while the consolute point (the point of intersection of the binodal curve and the rectilinear diameter) should be displaced towards the axis of the polymer with the lower lyophilicity. These features are valid for mixtures of proteins in a common solvent.

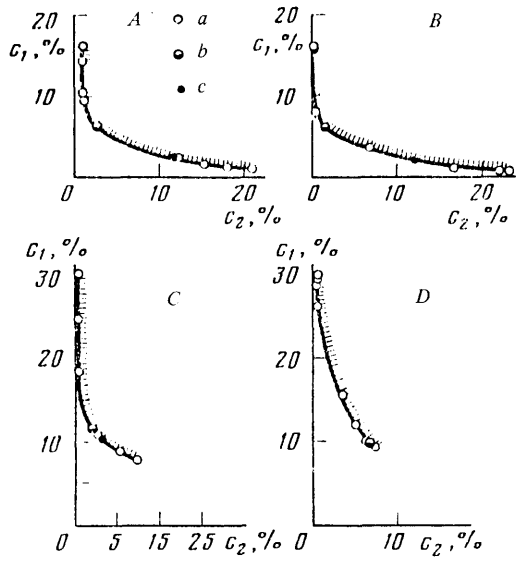

Figure 15. Phase diagrams for certain protein (1)–protein (2)–water systems: *A*) gelatin (1)–globulin fraction of fodder beans (2)–water (t = 40 °C, pH 7.0); *B*) gelatin (1)–11*S*-globulin from fodder beans (2)–water (t = 40 °C, pH 7.0); *C*) ovalbumin (1)–thermotropic ovalbumin cluster (2)–water (t = 20 °C, pH 6.8); *D*) bovine serum albumin (1)–thermotropic ovalbumin cluster (2)–water (t = 20 °C, pH 6.8); conditions in the preparation of the thermotropic ovalbumin cluster: temperature 100 °C, duration of heat treatment 60 min, protein concentration 5%, method of concentration—lyophilisation.

The above result shows that the equation of state indicated is applicable regardless of the model (freely jointed chains on a lattice[118,119]) on the basis of which it has been obtained.

The possibility of regulating the thermodynamic compatibility of proteins is of some interest. One of the effective ways of achieving such regulation is thermotropic aggregation of the protein. It is known[120] that heating above the denaturation temperature leads to the formation of soluble clusters of protein molecules when the concentration of the protein does not exceed the gel formation threshold.[121] The size, shape,[122] and probably the hydrophilic properties of the accessible surfaces of these clusters can be altered by varying the conditions in the heat treatment of the protein solution. The extent to which the heat treatment influences the compatibility of proteins is indicated by the phase diagrams *C* and *D* in Fig.15. In the native state BSA and ovalbumin are fully compatible in an aqueous medium. However, the thermotropic ovalbumin clusters are incompatible not only with BSA but also with native ovalbumin.

3. Practical Utilisation of Two-Phase Liquid Systems

(a) Concentration and purification of proteins. A low layer-formation threshold and a high ratio of the protein and polysaccharide concentrations at the consolute point are typical for the phase diagrams of protein–polysaccharide–water systems. In other words, the protein–polysaccharide–water systems separate into different phases which differ sharply in the concentrations of the macromolecular components, namely into a highly concentrated phase enriched in the protein (the polysaccharide content is not more than 0.5%) and a dilute polysaccharide phase. A new method of concentrating protein solutions, called membrane-free osmosis, is based on this phenomenon.[69] In particular, it has been used to concentrate proteins of defatted milk with the aid of apple pectin. The concentration of milk proteins to 30% is achieved at a polysaccharide concentration in the system of 1%. The high productivity, by virtue of the large area of the interface, the simplicity of the apparatus, and the relatively high energy efficiency may be included among the advantages of the process.

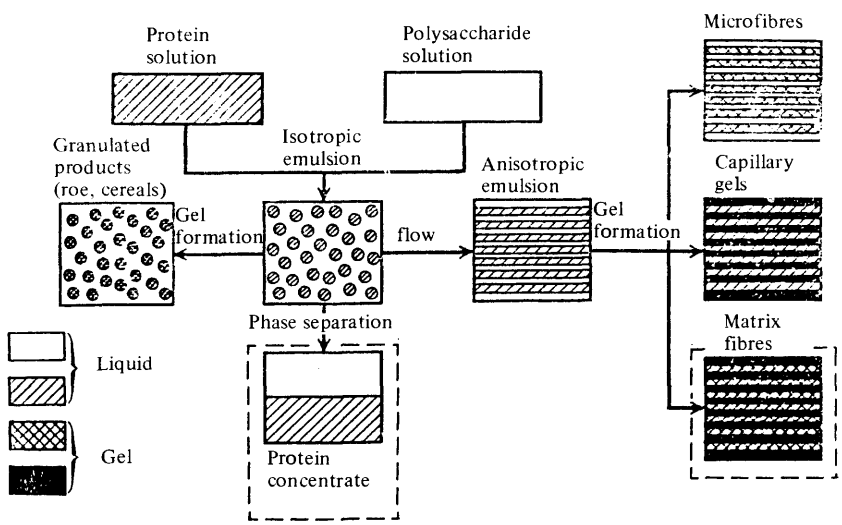

Figure 16. Scheme for the employment of two-phase protein–polysaccharide–water systems in the processing of protein.[1,66]

Yet another possibility of the practical utilisation of the phenomenon of the limited thermodynamic compatibility of proteins and polysaccharides in solution is based on the fact that protein–lipid complexes are less compatible with polysaccharides than lipid-free proteins. This effect has been used to remove lipids from the globulin fraction of baker's yeast proteins.[123,124] The lipid content in the protein preparation was thus reduced to 0.1%.

(b) The manufacture of new forms of food by processing two-phase liquid systems. The extensive possibilities for the preparation of NFP by processing two-phase liquid systems of the "water in water" type have been demonstrated in recent years. Such systems are formed by thermodynamically incompatible solutions of proteins and polysaccharides or different proteins. A general scheme for the processes involved in the processing of two-phase liquid systems to produce NFP[1,66] is illustrated in Fig.16. It includes the deformation of the two-phase liquid system in a flow and the conversion of one or both phases into a gel.

The possibility of attaining high degrees of deformation of the two-phase liquid system is ensured by the low interfacial tension; an approximate equality of the viscosities of the two phases is also necessary.[125] The ratio of the viscosities of the phases together with the dimensions of the particles of the disperse phase and the rate of shear determine the structure of the two-phase liquid systems in a stream and the possibility of processing them.[126]

On passing to the gel state in a flow, the particles of the disperse phase form protein microfibres. Depending on the volume fraction of the disperse phase, it is possible to obtain both short fibres and infinitely long fibres. In the latter case the formation of a gel is preceded by the coalescence of the deformed disperse particles. This process has been called spinning without a drawplate.[126] For high degrees of deformation, granulated products can be obtained in which the grains are anisodiametric to different extents.

When the dispersion medium is converted into a gel in a flow, gels filled with liquid cylinders oriented in the direction of the flow, the so-called gels with a capillary structure, are produced. The stability of these gels at right angles to the direction of orientation of the capillaries increases with increasing rate of shear.[125,127] For high degrees of filling, the continuous phase consists of the fibre cross-sections. Finally, there is a possibility that both phases of the deformed two-phase liquid system are converted into a gel. Gels filled with fibres oriented in the direction of the deformation, which are anisotropic in their mechanical properties, are obtained in this way.

All the principal versions of the processing of proteins in two-phase liquid systems under the conditions of high degrees of deformation of the disperse particles (not less than 10) are of practical importance in the preparation of analogues of meat products—fibres and textured materials.

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Photochemistry of Aliphatic and Aromatic Amines

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The luminescence spectroscopic properties and photochemical reactions of aliphatic and aromatic amines in liquid and solid solutions are examined. Attention is concentrated on the photochemical reactions of aromatic amines derived from aniline in liquid solutions. The mechanism of the photodissociation of the nitrogen-hydrogen and carbon-nitrogen bonds and the dependence of the luminescence spectroscopic properties of amines on their structure and on the positions of their energy levels in the lowest electronically excited states are discussed.
The bibliography includes 151 references.

CONTENTS

I. Introduction	1041
II. Aliphatic amines	1042
III. Aromatic amines	1045

I. INTRODUCTION

Much attention has been devoted recently to the study of the mechanisms of the photochemical processes involving aliphatic and aromatic amines not only because of the vigorous development of fundamental photochemical studies but also because of numerous investigations in adjacent branches of science and engineering (photobiology, photodegradation, and photostabilisation of polymers, theory of photographic processes, lasers based on organic compounds). The absorption bands of amines are as a rule located in the ultraviolet and in addition amines have low oxidation potentials. In view of these properties, aliphatic and aromatic amines are convenient models for the investigation of the mechanisms of photochemical processes and, in particular, of the quenching of fluorescence via electron transfer and for the investigation of donor–acceptor interactions in exciplexes.

The need for a detailed description of the reactivities of organic compounds in terms of different classes arises from the fact that photochemical behaviour is usually classified in terms of types of reactions: photodissociation (photocleavage), photosubstitution, photoaddition, photoisomerisation, and photorearrangements, as well as oxidation-reduction reactions (electron phototransfer). However, such studies are insufficient for the understanding of the reactivities of compounds of different types, particularly since in practice the converse problem frequently arises: it is necessary to know the photochemical properties of compounds of a definite class in order to foresee all the reactions possible under the given conditions.

The aim of the present review was to examine and summarise the results of studies of the photochemical and luminescence spectroscopic properties of aromatic and aliphatic amines. For this purpose, a classification of the photochemical properties of amines is proposed on the basis of ideas concerning the elementary photochemical processes and a scheme for the disposition of the lowest electronically excited states in specific systems has been constructed. The nature of the electronically excited state through which a photochemical reaction proceeds is discussed on the basis of kinetic data for the elementary processes.

The formation of exciplexes in the degradation of the electronic excitation energy has been studied in extremely great detail.[1-3] This review deals only with the mechanisms of the photochemical reactions of amine molecules in solutions (the mechanisms of the solid-phase reactions of these compounds have been studied fairly completely[4-13]). The data on the photolysis and, in particular, the luminescence of amines in the gas phase, which have been described systematically in a monograph,[7] are invoked only insofar as they are needed for the understanding of the photoprocesses in the condensed phase.

Table 1. The luminescence spectroscopic properties of aliphatic amines.

Amine	Solvent	λ_{abs}^{max}, nm	ϵ_{max}, litre mol^{-1} cm^{-1}	λ_{fl}^{max}, nm	φ_{fl}	τ_{fl}, ns	Refs.
Trimethylamine	—	198	3720	287	0.97	45	[31]
Diethylmethylamine	hexane	—	—	292	0.64	26.0	[33]
"	tetrahydrofuran	—	—	308	0.44	42	[33]
"	ether	—	—	340	0.14	48	[33]
Triethylamine	hexane	—	—	286	0.69	--	[33]
"	tetrahydrofuran	—	—	340	—	--	[38]
"	ether	—	—	310	—	—	[38]
4-Methylpiperidine	—	207	5500	290	0.95	60	[37]
4,*N*-Dimethylpiperidine	—	—	—	—	1.0	50	[37]
N-Methylmorpholine	—	204	4150	274	0.78	66	[37]

Notation: λ_{abs}^{max} and ε_{max} are the wavelength of the maximum in the absorption spectrum and the extinction coefficient and λ_{fl}^{max}, ϕ_{fl}, and τ_{fl} are the wavelength of the maximum in the fluorescence spectrum, the quantum yield, and the fluorescence lifetime.

II. ALIPHATIC AMINES

1. Absorption Spectra

Bands of moderate intensity with a maximum at ~200 nm (Table 1) are observed in the ultraviolet absorption spectra of the simplest aliphatic amines (methyl- and ethyl-amines). Previously it was regarded as an established fact that the long-wavelength absorption band of aliphatic amines corresponds to the $n \rightarrow \sigma^*$ transition and is therefore absent from the spectra of acid solutions since the nitrogen atom in the cation has no non-bonding n electrons.[14-21] Within the framework of this type of explanation and on the basis of quantum-chemical calculations, it has been suggested[14] that the unshared electron pair in the molecules of ammonia and alkylamines is located in the *sp*-hybrid atomic orbital (AO) located along the symmetry axis of the molecule. The band corresponding to the $n \rightarrow \sigma^*$ transition in the absorption spectra of such molecules should be fairly intense.[22-31] Recent calculations[19-23] have shown that all the lowest electronically excited states of ammonia and primary amines are of the Rydberg type (Table 2) (the assignment of the long-wavelength absorption bands to the $\sigma \rightarrow \sigma^*$ and $n \rightarrow \sigma^*$ transitions in alkylamines is erroneous[31]). The simplest primary amines (methylamine and ethylamine) have a lowest Rydberg n, 3*s* state in which the predissociative decomposition of the N–H bond takes place.[23]

Table 2. The transitions for ABCO and ABCU.[39]

Transition	n	Orbital*
ABCU		
$S_1 \leftarrow S_0$	3	3*s*
$S_2 \leftarrow S_0$	3	3*p*
$S_3 \leftarrow S_0$	3	3*d*
$S_3 \leftarrow S_0$	4	4*s*
$S_4 \leftarrow S_0$	4	4*p*
ABCO		
$S_1 \leftarrow S_0$	3	3*s*
$S_2 \leftarrow S_0$	3	3*p*
$S_3 \leftarrow S_0$	4	4*s*

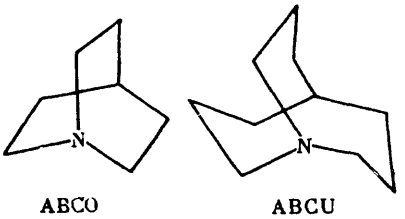
*Only the Rydberg orbitals are presented.

2. Luminescence Properties

Tertiary aliphatic amines fluoresce in the gas phase and in solution,[12,32,33] while primary and secondary amines do not. The fluorescence of the simplest tertiary amines (trimethylamine and tri-n-propylamine) under the influence of light at a wavelength of 206.2 nm takes place either in the σ^* or Rydberg state.[32] The absence of fluorescence in primary and secondary amines in the gas phase is associated with their effective deactivation via predissociation, which takes place only in compounds where hydrogen (or deuterium) is bonded directly to the nitrogen.[32-42]

In the absence of steric perturbations, the configuration of the molecules of saturated tertiary amines (in which the unshared electron pair of the nitrogen plays the role of the chromophore) in the equilibrium excited singlet state is planar (and not tetrahedral as in the ground state).[39]

The nature of the atomic orbitals in which n electrons are excited on irradiation has been determined for symmetrical amines derived from 1-azabicyclo[2,2,2]octane (ABCO) and 1-azabicyclo[3,3,3]undecane (ABCU) on the basis of the magnitude of the quantum defect (Table 2); it was found that all three long-wavelength bands are of the Rydberg type for these substances.[39-42]



ABCO ABCU

An intense bathochromic shift of the fluorescence spectra with increasing solvent polarity is characteristic of all aliphatic amines (Table 2); the long-wavelength bands of the fluorescence excitation and absorption spectra then remain

unaltered (at 77 K a shift of the above type is not observed in a frozen matrix).[42] The shift is associated, according to Muto et al.,[42] with the change in the nature of the lowest electronically excited state of amines from the Franck–Condon state, corresponding to the first absorption band of the σ* type, to the Rydberg 3s state, which is significantly stabilised under the influence of the solvent as a result of the ion–dipole interaction of the nucleus of the cation in the Rydberg 3s state with a solvent molecule. A model of the solvated Rydberg state,[42] in which the orbital of the excited amine electron passes through the closest solvent molecules has in fact been developed on the basis of the fluorescence data for aliphatic amines. Thus the solvated Rydberg state consists, according to Nakato et al.,[43] of a cation–electron pair linked by Coulombic forces.

The role of the solvated Rydberg state in the bathochromic shift of the fluorescence spectrum of diethylmethylamine in a polar solvent has been noted in a recently published communication.[33]

An *ab initio* quantum-chemical calculation of the energies of the lowest electronic transitions in trimethylamine, ABCO, and diazabicyclo[2,2,2]octane (DABCO) showed[34] that all these states are fully of the Rydberg type (no valence states with energies below 6.4 eV have been found), although it had been assumed earlier[41] that two long-wavelength bands in the absorption spectra of dialkylamines are associated with the $n \rightarrow \sigma^*$ transition. It has also been noted that in the case of saturated amines there can be no mixing of the excited valence states with the Rydberg states (at least for the amines in which excitation entails an insignificant alteration of the molecular geometry[34]).

3. Photochemical Properties

(a) Primary amines

The photochemical properties of all the aliphatic amines, except tertiary amines, are determined by the lability of their N–H bonds. Under the influence of light with $\lambda < 240$ nm, aliphatic amines in hexane decompose with formation of gaseous products and hex-1-ene. The primary step in the photolysis is the dissociation of the N–H bond:[15]

$$RNH_2 + h\nu \rightarrow R\dot{N}H + H. \quad (1)$$

The quantum yields in the photodecomposition of amines in hexane are listed in Table 3; they depend only slightly on the concentration of the amines and increase insignificantly with increased temperature.

In polar solvents (for example, in water) the dissociation of the C–N bond becomes possible because the homolytic dissociation of the N–H bond is hindered owing to the considerable solvation of the amine molecules:[16,17]

$$RNH_2 + h\nu \rightarrow \dot{R} + \dot{N}H_2. \quad (2)$$

The photodecomposition quantum yield is then found to be less than in hexane (Table 4) and the photolysis products are ammonia and alcohols. In water the yield in the photodecomposition of amines increases sharply with increasing pH.

The mechanism of the liquid-phase photolysis of aliphatic amines has been studied in greatest detail for solutions of cyclohexyl- and cyclopentyl-amines in cyclohexane and cyclopentane and also of n-hexylamine in hexane.[18] The products of the photolysis of cyclohexylamine are cyclohexylcyclohexane and ammonia and those of the photolysis of cyclopentylamine are cyclopentylcyclopentane, *N*-cyclopentylidenecyclopentylamine, and dicyclopentylamine. The primary processes occurring under these conditions can be illustrated schematically in the following manner:

$$RR'CHNH_2 \xrightarrow{h\nu} \begin{cases} \rightarrow RR'CH\dot{N}H + H; & (3) \\ \rightarrow RR'\dot{C}H + \dot{N}H_2; & (4) \\ \rightarrow RR'\dot{C}NH_2 + H; & (5) \\ \rightarrow RR'C{=}NH + H_2. & (6) \end{cases}$$

Table 3. The quantum yields in the photochemical decomposition of amines in hexane (ϕ_1) and water (ϕ_2)*.

Amine	φ_1	φ_2	Amine	φ_1	φ_2
Isopropylamine	0.100	0.049	n-Pentylamine	0.052	0.037
n-Propylamine	0.079	0.039	n-Hexylamine	0.064	0.038
Isobutylamine	0.092	0.046	n-Heptylamine	0.036	0.025
n-Butylamine	0.082	0.042	n-Octylamine	0.039	0.027
Isopentylamine	0.086	0.050			

*The amine concentration was 10^{-3} M; the irradiation was carried out at a wavelength of 230–240 nm.

Table 4. The energy levels (E, eV), the oscillator strengths (f), and the wave functions for the aniline molecule (according to the data of Kimura et al.[47]

Level	E_{calc} (gas phase)	E_{exp} (gas phase)	E_{exp} (in hexane)	f_{calc}	f^*_{exp} (in hexane)
W_1	4.72	4.40	4.32	0.021	0.028
W_2	5.42	5.39	5.31	0.174	0.144
W_3	6.42	6.40	6.32	0.416	0.510
W_4	6.86	6.88	7.06	0.505	0.570
W_5	8.04	7.87	—	0.745	0.68
W_6	8.05	7.87	—	0.416	0.68

*Data of Kimura and Nagakura.[55]

The relative contributions of reactions (3)–(6) for each compound are determined by the stability of the corresponding alkyl radicals. For cyclohexylamine, the principal primary photochemical process is the dissociation of the C–NH_2 bond [reaction (4)], which is followed by the interaction with the solvent:

$$NH_2 + C_6H_{12} \rightarrow \dot{C}_6H_{11} + NH_3;$$

$$2C_6H_{11} \rightarrow C_{12}H_{22}. \quad (7)$$

In the case of cyclopentylamine dissociation of the N–H bond [reaction (3)] plays the main role. On photoirradiation of n-hexylamine in cyclohexane the main product is *N*-(1-hexylidene)-n-hexylamine together with bicyclohexyl and cyclohexylamine; here too the primary photochemical process is reaction (3) involving the elimination of a hydrogen atom.[18]

The almost complete lack of data on the quantum yields of the primary photochemical processes in the photolysis of aliphatic amines in the liquid phase is noteworthy. It is

apparently due to the difficulty of the quantitative determination of the yields of the aminyl radical formed.

In contrast to the processes in the gas phase, the nature of the primary process in solutions has been little investigated: for example, it has not been established for virtually any system which of the bonds in the molecule is dissociated and what is the probability of the process; the extent of other radiative and non-radiative pathways leading to the dissipation of the electronic excitation energy in solutions of aliphatic amines are also unknown. The secondary photochemical reactions, i.e. the further reactions of the compounds arising in reactions (3)–(6) with formation of stable final products, have not been investigated in extremely great detail for aliphatic amines. The present level of knowledge is such that the nature of the final photoproducts and the relative yields can be predicted for any aliphatic amines in the usual solvents.

In the photolysis of amines in the gas phase the quantum yields in the formation of products have been measured for a series of primary photochemical processes[44–46] (one should bear in mind that only the yields in the formation of the final products were measured and the efficiency of the primary photochemical processes was inferred only from indirect data).

For example, it has been suggested[44] that methylamine undergoes photodissociation under the influence of radiation with $\lambda = 184.9$ nm:

$$CH_3NH_2 + h\nu \rightarrow CH_3\dot{N}H^* + H.$$

The quantum yield is unity and the aminyl radical formed is in an electronically excited state, decomposing further in accordance with the scheme

$$CH_3NH^* \longrightarrow H + H_2C{=}NH.$$

As a result, the quantum yield for the formation of hydrogen in the photolysis of gaseous CH_3NH_2 exceeds unity.

The quantum yields of the photochemical reaction of CH_3NH_2 in the gas phase depend strongly on the excitation wavelength[44] and the excitation of the methylamine molecule to the S_3 state entails the formation of CN and HCN via the mechanism

$$CH_3NH_2 \xrightarrow{h\nu} \begin{cases} \xrightarrow{\alpha} CH_3\dot{N}H^* + H \rightarrow H + H_2C{=}NH; \\ \xrightarrow{1-\alpha} CH_2NH^* + H_2 \rightarrow H_2 + HCN^*; \end{cases}$$

$$HCN^* \longrightarrow \begin{cases} \xrightarrow{\beta} H + \dot{C}N; \\ \xrightarrow{1-\beta} HCN, \end{cases}$$

where $\alpha = 0.59$ and $\beta = 0.44$.

As regards the photolysis of amines in the solid phase, there has been only one communication[40] stating that hydrogen atoms are ejected into the gas phase in the photolysis of frozen methylamine.

The first attempts to interpret theoretically the accumulated experimental data on the photochemical reactions of aliphatic amines and to answer the important question why the dissociation of the N–H bond in gaseous amines and not the C–N bond is most likely have been made only recently.[23] By means of non-empirical calculations, it has been possible to show[23] that the lowest excited singlet state of methylamine (the Rydberg n, $3s$ state) is capable of an adiabatic transition to the valence states of the radical products (CH_3NH + H or CH_3 + NH_2). As for NH_2, the $3s$ orbitals then lose their Rydberg character and are localised at the H atom (which leads to the dissociation of the N–H bond). In general, the transition to the Rydberg states takes place as follows: $3s \rightarrow 3s$, $\sigma^* \rightarrow 1s$.

The bond dissociation in systems of this kind thus proceeds in such a way that n, $3s$ states are converted into n, σ^* states (here σ^* refers to N–H or C–N bonds) at a certain point on moving along the reaction coordinate (i.e. on "extension" of the N–H or C–N bond). The potential energy surface of the molecule in the n, $3s$ state has a shallow minimum corresponding to such dissociation or has none at all. However, higher Rydberg states (for example, n, $3p$) have deeper minima and should be correlated with higher (usually Rydberg) states of the products. The behaviour of the molecules in the n, $3s$ state in the bond dissociation process should therefore differ from their behaviour in higher Rydberg states for which the H_2 elimination process is possible.

The potential energy surfaces for the dissociation of the N–H and C–N bonds in the n, $3s$ state for CH_3NH_2 have a minimum in the region of the Franck–Condon geometry; the dissociation of the N–H bond therefore takes place in the state to which the system is excited.

The C–N bond dissociation energy in methylamine is twice as high as the N–H bond dissociation energy.[13] However, even when the energy barrier is the same, the N–H bond should have been ruptured much more readily because this process can take place fairly effectively via tunnelling (which is feasible precisely for shallow minima of the kind which obtain in the n,$3s$ state). This in fact explains the finding that the primary photochemical process involving methylamine (and many other primary amines) in the gas phase is the dissociation of the N–H bond and this is why triethylamine (and other tertiary amines) are relatively stable on excitation by radiation with a wavelength in the region of the 0–0 band in the absorption spectrum.

(b) Secondary amines

The main products of the photolysis of ethylmethylamine in hydrocarbon solvents are hydrogen, unsaturated compounds, small amounts of methane, and a nitrogen-containing polymer.[59]

Photolysis of pure liquid diethylamine by the radiation emitted by a high-pressure mercury lamp in the absence of oxygen leads to the formation of mainly *N*-butenylidene(2-ethyl-2-butyl)ethylamine (yield in excess of 70%) and also a mixture of the *meso*-racemates of *NN*-diethyl-2,3-butylenediamine, tetraethylhydrazine and 1,3-diethyl-2,4,5-trimethylimidazoline.[20,21] The reaction mechanism involves the photodissociation of the α-hydrogen atom and the formation of the radical $CH_3\dot{C}HCNC_2H_5$. The disproportionation of this radical leads to the formation of *N*-ethylideneamine, while dimerisation produces *NN*-diethyl-2,3-butylenediamine; the interaction of these two products affords 1,3-diethyl-2,4,5-trimethylimidazoline:

$$2CH_3CHNHC_2H_5 \longrightarrow \begin{cases} \rightarrow CH_3CH{=}NC_2H_5 + (C_2H_5)_2NH; \\ \rightarrow CH_3\underset{\displaystyle CH_3\dot{C}HNHC_2H_5}{CHNHC_2H_5}; \end{cases}$$

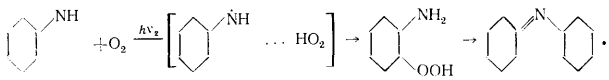
$$2CH_3CH{=}NC_2H_5 \rightarrow \underset{\displaystyle CH_2CH{=}NC_2H_5}{CH_3CHNHC_2H_5} \rightarrow CH_3CH{=}CHCH{-}NC_2H_5.$$

The presence of hydrazine among the reaction products means that the primary step in the photolysis is the abstraction of a hydrogen atom from the nitrogen, i.e. the dissociation of the N–H bond.

It is noteworthy that one cannot postulate the photodissociation of the pure compound on photoirradiation, as was done by Allan and Swan,[20] because at the given concentration

of the test substance it is in principle impossible to distinguish true photodissociation from the processes occurring on self-quenching.

The photoirradiation of solutions of amines in the presence of oxygen leads to a variety of products, which are obtained on decomposition of the hydroperoxide formed initially.[21] The excited state of the contact charge-transfer complex between the amine and oxygen arises in the first stage of photolysis[24-28] and then decomposes with formation of a hydroperoxide, which is converted into the final products:



The photoirradiation of solutions of di-n-hexylamine, dicyclohexylamine, and cyclohexyl-n-hexylamine in cyclohexane (10^{-2} M) in the absence of oxygen at 18 °C leads to the formation of the corresponding imines in preparative yields of 89–91%[28,29] (for the first compound, the product is *N*-n-hexylidene-n-hexylamine together with cyclohexylcyclohexane and n-hexylamine, while for the second compound the product is *N*-cyclohexylidenecylcohexylamine together with cyclohexylcyclohexane and cyclohexylamine). The entire photochemical reaction includes the following processes:

$$R_2NH + h\nu \rightarrow [R_2\dot{N} + H];$$
$$[R_2\dot{N} + H] \rightarrow R'CH{=}NR + H_2;$$
$$R_2NH + H \rightarrow R_2\dot{N} + H_2;$$
$$2R_2\dot{N} \rightarrow R'CH{=}NR + R_2NH.$$

In the review of von Sonntag and Schueman[12] the formation of hydrogen and imines in the photolysis of dihexylamines has been erroneously attributed to the H_2 elimination reaction.

The photoirradiation of a solution of dimethylamine in n-nonane (at a concentration in excess of 1 M) at 35 °C in the absence of oxygen leads to the formation of mainly *NNN'N'*-tetramethyldiaminomethane.[23] In addition, a small amount of methylamine and microamounts of *NNN*-triemthyldiaminomethane as well as tetramethylhydrazine are produced. The overall process mechanism includes the following stages:

$$\begin{gathered}(CH_3)_2NH + h\nu \rightarrow [(CH_3)_2\dot{N} + H];\\ [(CH_3)_2\dot{N} + H] \rightarrow H_2 + CH_3N{=}CH_2;\\ 2(CH_3)_2\dot{N} \rightarrow (CH_3)_2NCH_2N(CH_3)_2 + CH_3N{=}CH_2;\\ (CH_3)_2NH + H_2C{=}NCH_3 \rightarrow (CH_3)_2NCH_2NHCH_3.\end{gathered} \quad (8)$$

Photoirradiation of solutions of dimethylamine in chloroform and other organochlorine solvents also leads to the formation of aminyl radicals, but as a result of the photodissociation of the intermediate charge-transfer complex and not as a result of direct photodissociation:[24-26]

$$(CH_3)_2NH \cdot CCl_4 \xrightarrow{h\nu} Cl_3\dot{C} + [(CH_3)_2NH^+]Cl^-;$$
$$[(CH_3)_2NH^+] + (CH_3)_2NH \rightarrow (CH_3)_2NH \cdot HCl + (CH_3)_2\dot{N}.$$

The aminium radical-cation abstracts a hydrogen atom from the initial compound with formation of $(CH_3)_2\dot{N}$. This results in the formation of the dimer $(CH_3)_2NCH_2N(CH_3)_2$ and methylamine in this case too, but via different mechanisms.

Thus, in contrast to the photolysis of dimethylamine in the gas phase,[17,24-26] in organic solvents the recombination of aminyl radicals with formation of hydrazine derivatives takes place to an extremely significant extent. The almost complete absence of *NN*-dimethyldiaminomethane among the photolysis products means, according to the authors,[24] that the mechanism of the photolysis of dimethylamine is different to that postulated by Allan and Swan[20] and does not include the stage involving the formation of a C-centred radical (in addition, the α-aminoalkyl radical formed shows a tendency to recombine but not disproportionate). It is noteworthy that, according to the data of Kassab et al.,[23] obtained in the photolysis of a 1 M solution of dimethylamine, the photolysis products do not contain an imine having the structure R'HC = NR, while according to Hadley and Volman[30] precisely these amines are the main final photolysis products.

This discrepancy is apparently associated with the fact that at fairly high temperatures the imines are effectively converted into other products as a result of the reaction with the initial amine [reaction (8)] and also the fact that the imines investigated by Hadley and Volman[30] are less reactive in the nucleophilic addition of amines owing to the steric hindrance introduced by the bulky hexyl substituent.

The photodissociation of the N–H bond and the formation of the aminyl radical $(CH_3)_2\dot{N}$ in the photolysis of dimethylamine have been confirmed by the direct detection of this radical by EPR at 77 K[31,32] (the $CH_3NH\dot{C}H_2$ radical was not then detected).

In the photolysis of solutions of primary and secondary amines in non-polar solvents, the dissociation of the N–H bond is the main process for n-alkyl derivatives; the composition of the stable products is then determined by the reactivity of the aminyl radical formed and the concentration of the amine (i.e. the ratio of the rates of radical disproportionation and recombination) and also by the interaction of the radicals with the amine itself. In the photolysis of cyclic amines in more polar solvents, the probability of the dissociation of the C–N bond is greater, which leads to the appearance of products such as ammonia and bicyclohexyl (for cyclohexylamine).

(c) Tertiary amines

The photolysis of pure triethylamine by the light of a moderate pressure mercury lamp in the absence of oxygen leads to the formation of the *meso*-racemic mixture of *NNN'N'*-tetraethyl-2,3-butylenediamine and *NN*-diethyl-2,3-butylenediamine,[20] as well as small amounts of 1,3-diethyl-2,4,5-trimethylimidazoline and tetraethylhydrazine. The authors believe that the primary photochemical steps in this case are both the dissociation of the C–H bond with formation of the radical $CH_3\dot{C}HN(C_2H_5)_2$ and the dissociation of the C–N bond with formation of the radical $(C_2H_5)_2\dot{N}$, which is converted into diethylamine by abstracting hydrogen; diethylamine undergoes in its turn the photochemical decomposition described above.

III. AROMATIC AMINES

1. Absorption Spectra

The ultraviolet absorption spectra of the simplest aromatic amines (aniline and its derivatives) both in the gas phase and in solution have been investigated in fair detail.[47-55] The ultraviolet absorption spectra of aniline vapour clearly manifest five bands, three of which correspond to benzene absorption bands; at least two of the five bands are due to intramolecular charge transfer from the amino-group to the ring.[47]

Quantum-chemical calculations make it possible to interpret in detail the absorption spectra of aniline (Table 4). The wave functions for the excited states of aniline in the CNDO/S method were set up using singly excited electronic configurations of the π,π* aromati ccomponent of the aniline molecule and configurations with charge transfer from the orbitals of the unshared electron pair of the nitrogen atom to the antibonding orbitals of the aromatic ring (these configurations

correspond to the $l \rightarrow a_\pi$ transitions in Kasha's terminology [47,50]

Seven electronic configurations have been used to construct the wave functions $\Psi_0 - \Psi_b$: thsoe of the ground state, two charge-transfer states, and four locally excited states corresponding to the $A_{1g} \rightarrow B_{2u}$, $A_{1g} \rightarrow B_{1u}$, and $A_{1g} \rightarrow E_{1u}$ transitions in the benzene molecule. It follows from these calculations that the transition to the S_1 state in aniline corresponds to the transition to the B_{2u} state of the benzene ring; the contributions of charge-transfer configurations to this S_1 state are 22% for aniline and 36% for *NN*-dimethylaniline. The contribution of the charge-transfer configurations to the W_2 state of aniline is more than 50% (Table 4); thus the transitions in the aniline molecule cannot be regarded as simply the benzene transitions perturbed by the presence of the attached amino-group.[56]

Table 5. The calculated and experimental energies (E) and oscillator strengths (f) for the long-wavelength transitions of aniline derivatives.[47,55]

Transition	E, eV		f	
	calc.	expt.	calc.	expt.
		N-Methylaniline		
$W_0 \rightarrow W_1$	4.66	4.37	0.024	0.031
$W_0 \rightarrow W_2$	5.28	5.20	0.179	0.190
$W_0 \rightarrow W_3$	6.32	6.31	0.330	0.478
$W_0 \rightarrow W_4$	6.85	6.88	0.440	0.556
$W_0 \rightarrow W_5$	7.95	7.80	0.826	0.71
$W_0 \rightarrow W_6$	7.97		0.472	
		N-Ethylaniline		
$W_0 \rightarrow W_1$	4.63	4.34	0.025	0.048
$W_0 \rightarrow W_2$	5.22	5.17	0.181	0.230
$W_0 \rightarrow W_3$	6.28	6.28	0.3 4	0.450
$W_0 \rightarrow W_4$	6.85	6.88	0.426	0.530
$W_0 \rightarrow W_5$	7.92	7.75	0.850	0 77
$W_0 \rightarrow W_6$	7.95		0.475	
		NN-Dimethylaniline		
$W_0 \rightarrow W_1$	4.61	4.30	0.026	0.044
$W_0 \rightarrow W_2$	5.17	5.15	0.182	0.256
$W_0 \rightarrow W_3$	6.25	6.25	0.279	0.350
$W_0 \rightarrow W_4$	6.85	6.88	0.409	0.575
$W_0 \rightarrow W_5$	7.90	7.68	0.875	0.81
$W_0 \rightarrow W_6$	7.93		0.497	
		NN-Diethylaniline		
$W_0 \rightarrow W_1$	4.55	4.21	0.027	0.051
$W_0 \rightarrow W_2$	5.06	5.00	0.186	0.280
$W_0 \rightarrow W_3$	6.18	6.25	0.233	0.318
$W_0 \rightarrow W_4$	6.84	6.88	0.377	0.535
$W_0 \rightarrow W_5$	7.86	7.62	0.920	0.88
$W_0 \rightarrow W_6$	7.89		0.525	

It is believed[47-49,55] that all the intense absorption bands of aniline and its simplest derivatives (*N*-methylaniline, *N*-ethylaniline, *NN*-dimethylaniline, *NN*-diethylaniline, and *N*,n-butylaniline) with energies below 6.2 eV are due to $\pi-\pi^*$ transitions (Table 5). The additional bands in the region of 230 nm in the spectra of *N*-methyl-, *N*-ethyl-, and *N*-butyl-anilines have been tentatively assigned[99] to the $n \rightarrow \sigma^*$ transition, because the bands corresponding to the $n \rightarrow \sigma^*$ transitions are characteristic of saturated aliphatic amines precisely in the region of ~200 nm[57] (see the discussion of this problem below). Despite the convincing agreement between the calculated and measured transition energies[47,55] (Tables 4 and 5), an unambiguous interpretation of the electronic states of amines remains unattainable because of the necessity for the complete separation of the contributions by the σ and π orbitals, since the amine molecules are nonplanar.[58]

On the basis of calculations[49] by the PPP method taking into account the configuration interaction (in relation to aniline, β-naphthylamine, β-aminoanthracene, vinylamine, and butadienylamine), it has been shown that the excited states of many aromatic and unsaturated amines cannot be classified as "pure" π,π^* or l,a_π states but are mixed [it has been suggested that they be designated by $S(\pi l,\ \pi^*)$ and $T(\pi l\pi)$]. With increase of the Ar–NH_2 bond length, "pure" l,a_π states can appear among the excited states of these amines†.

The increase in the size of the π system is accompanied by a decrease of the contribution of the l,a_π state to the wave functions of the lowest excited states because the vibrational structure is revealed more clearly in the absorption spectra of amines with an extensive system of π-bonds.

Furthermore, comparison of the rotational constants for the S_1 state of aniline and other benzene derivatives[68] makes it possible to establish precisely that the C–N bond in the molecule of aniline in the S_1 state is shorter by 0.08 Å than in the S_0 state, because the conjugation between the unshared electron pair in the $2p_x$ orbital and the π electrons of the ring is stronger in the S_1 state.

By measuring the absorption and magnetic circular dichroism spectra of aniline and *NN*-diethylaniline in solution in the gas phase, it has been possible to establish[52] that the absorption bands of these compounds in the range 46000 to 60000 cm^{-1} correspond to the Rydberg transitions.

The absorption spectrum of aniline vapour contains a 0–0 band, corresponding to the $S_1 \leftarrow S_0$ transition and located at 46530 cm^{-1}, as well as a vibrational progression at 490 cm^{-1}. These bands are absent from the spectra of the solutions and films at 77 K; on these grounds, there are attributed to Rydberg transitions, like the bands at 53270 and 56660 cm^{-1}. All these bands are described by the Rydberg formula

$$h\nu = 62\,170 - R/(n-\delta)^2,$$

where 62170 cm^{-1} is the first (adiabatic) ionisation potential of aniline. The quantum defect, which amounts to $\delta = 0.53$, shows that the bands belong to the *np* series.

In contrast to aniline, Rydberg transitions not only of the *p* type but also of the *s* type (corresponding to the first ionisation potential) can be clearly observed for *NN*-diethylaniline, which is associated with the fact that the highest occupied orbital in *NN*-diethylaniline has a different character—this is predominantly the *n* orbital of the substituent (the amino-group).

Thus Rydberg transitions appear at 47180 cm^{-1} in the spectrum of aniline and at ~36520, 38880, and 42000 cm^{-1} for *NN*-diethylaniline;[52] consequently the appearance of low-lying Rydberg states, due to the change in the nature of the highest occupied molecular orbitals, may be expected for aniline derivatives with electron-donating substituents (particularly in solution).

Previously it was thought to be established that the oscillator strengths of dialkylanilines,[59] corresponding to the four long-wavelength absorption bands, are proportional to

† Precisely the involvement of the l,a_π state in the establishment of the excited states explains the spreading of the absorption bands of the amines (compared with the bands in the spectra of hydrocarbons having a vibrational structure), because the change in the C = N bond length on excitation is in fact associated with these states.

$\cos^2\alpha$, where α is the angle between the plane of the amino-group and that of the benzene ring (the so-called "$\cos^2$ law"). This was deduced by Platt on the basis of the hypothesis that the dipole moment of the transition is proportional to the resonance energy, which is in its turn proportional to the overlap integral of the orbitals of the amino-group and the ring and hence to the angle α. However, the resonance energy for 5-cyano-*N*-methylindoline and all other indoline derivatives investigated is much higher than for methyl- or diethyl-aniline, although the oscillator strength of the long-wavelength transition is much lower for indoline derivatives.[59-61]

It is believed[62] that this discrepancy is caused by the mixing of the lowest charge-transfer states of these compounds with locally excited states: it has been shown that the energy of the lowest state of aniline hardly changes when the molecule is "twisted"[63] and the observed bathochromic shift of the absorption band is a consequence of the decreased energies of charge-transfer transitions. For low values of α, the mixing is slight and the usual $f \propto \cos^2\alpha$ relation is observed; for high values of α, there is a deviation from the relation caused by the contribution of the charge-transfer state.

According to Frolen and Goodman,[63] the $f \propto \cos^2\alpha$ law is valid only in the range of values of α amounting to ~30–90°; for smaller angles, one must use the formula

$$(\epsilon_{corr} - \epsilon_{min})/(\epsilon_0 - \epsilon_{min}) = \cos^2\alpha,$$

where ε_{corr} is the extinction coefficient at the maximum corrected for the non-steric influence of the substituents and ε_0 and ε_{min} are the maximum and the minimum values of ε respectively.

2. Luminescence Properties

All aromatic amines fluoresce in liquid solutions and hardly phosphoresce in frozen matrices;[62-91] examples are presented in Table 6.

The dependence of the fluorescence spectra of aniline on solvent polarity has been studied in detail and it has been shown that, with increased solvent polarity, the maximum of the fluorescence spectrum shifts from 315 nm in cyclohexane to 342 nm in water.[53] In hydroxylated solvents 1:1 complexes are formed with a hydrogen bond between the hydrogen of the hydroxyl and the unshared electron pair of aniline; an increase of solvent polarity leads to the "blocking" of the unshared electron pair of nitrogen, as a result of which the luminescence transition becomes close to the $n \rightarrow \pi^*$ type and the fluorescence quantum yield is correspondingly reduced.[65]

The fluorescent state of the β-naphthylamine molecule corresponds to the $'L_b$ state of naphthalene. The absorption band corresponding to this transition lies 6000 cm^{-1} below the band corresponding to the $'L_a$ state[148] (Table 6).

The first absorption band in the spectrum of α-naphthylamine consists of two unresolved components corresponding to transitions to the modified $'L_a$ and $'L_b$ states of naphthalene. The shoulder in the region of 30000 cm^{-1} in the absorption spectrum of its solution in cyclohexane corresponds to the transition to the $'L_b$ state.

Two features are characteristic of the luminescence properties of naphthylamines: an appreciable bathochromic shift of the fluorescence spectra in polar solvents while the fluorescence excitation spectrum remains unchanged and a significant discrepancy between the calculated and experimental fluorescence lifetimes.[148] It has been observed that the excitation of β-naphthylamine entails an increase of the dipole moment by 3.5 D, while the dipole moment of α-naphthylamine increases by 1.9–2.5 D. The increase of the dipole moment on excitation is caused by charge transfer from the nitrogen of the amino-group to the ring; the amino-group then undergoes a change in its conformation from the tetrahedral sp^3 conformation in the ground state to the trigonal sp^2 conformation in the excited state.[148] The equilibrium excited state is characterised by a greater degree of charge transfer than the Franck–Condon state, and the probability of a transition from this state is therefore greater than the probability calculated from the absorption spectra. This is why the experimental fluorescence lifetimes $\tau = \tau_{fl}/\phi$ are smaller than those calculated from the absorption spectrum.

Analogous results for α-naphthylamine have been again obtained recently and quite independently.[147] The authors investigated the kinetics of the quenching of the fluorescence and the shift of the fluorescence band as a function of solvent polarity and concluded that the $'L_a$ and $'L_b$ states of α-naphthylamine undergo an inversion in polar solvents. According to the authors,[147] the anomalous bathochromic shift of the fluorescence spectra of α-naphthylamine in polar solvents (even in frozen glasses) is associated with two mechanisms for relaxation of the Franck–Condon state: a change in the conformation of the amino-group and the relaxation of the solvent dipole relative to the increased amine dipole in the excited state, which leads to an increase of the contribution of the $'L_a$ charge-transfer state in polar solvents. The observed dependence of the bathochromic shift on solvent viscosity and temperature can be explained by the operation of the solvent dipole relaxation mechanism.

A characteristic feature of all aromatic amines, which leads to a change in their absorption spectra and to the quenching of their fluorescence, is the formation of hydrogen bonds with proton acceptors.[67] In the ground state the hydrogen bond between amines and proton acceptors is frequently very weak (for example, the equilibrium constant for the hydrogen-bonded complex between 1-aminopyrene and pyridine in hexane is 3 litre mol^{-1}); in polar solvents the hydrogen bonds are even weaker by virtue of the solvation of the amine and acceptor molecules. In the S_1 state amines form hydrogen bonds much more vigorously; the formation of a complex is manifested by the bathochromic shift of the absorption spectra.

It has been established by picosecond laser photolysis[114] that the excitation of such hydrogen-bonded complexes leads to charge transfer between the donor and acceptor and equilibrium between the locally excited donor and the charge-transfer complex (CTC) (D – H...A and $D^+ - H...A^-$) is established over a period shorter than 6 ps.

It is believed[114] that the fluorescence of amines in hydrogen-bonded complexes with pyridine is quenched as a result of the formation of short-lived non-fluorescent CTC on excitation of the hydrogen-bonded donor (amine)–acceptor (pyridine) pair.

(a) Acid–base properties in the ground and excited states

The luminescence properties of aromatic amines are closely related to their acid–base properties, namely all aromatic amines are weak bases. When aniline and aminoanthracenes are protonated, the perturbing influence of the amino-groups on the aromatic ring is reduced to a minimum and the absorption spectrum of the $C_6H_5NH_3^+$ ion in alcohol is therefore almost identical with the benzene spectrum,[69] while the spectra of the cations of aminoanthracenes are almost identical with the spectrum of anthracene.

The anilinium ion fluoresces and phosphoresces in the ether–isopentane–ethanol mixture (EPA) at 80 K and at room temperature;[22] the positions of the maxima of the 0–0 band at 80 K in EPA are illustrated below:

	Aniline	Anilinium ion
Absorption	35502	37497
Fluorescence	29620	37580
Phosphorescence	24535	29470

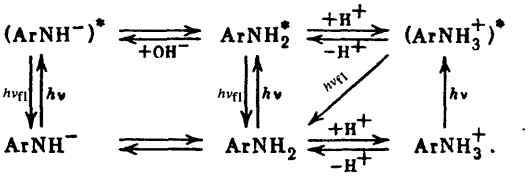
Table 6. The luminescence spectroscopic properties of amines.

Amine	Solvent	ν_{abs}, cm^{-1}	ϵ_{max}	ν_{fl}, cm^{-1}	φ_{fl}	τ_{fl}, ns	E_{0-0}, cm^{-1}	φ_{ISC}	Refs.
Aniline	hexane	34 800	1 760	31 750	0.17	3.9	32 937	0.75	[64]
"	"	34 602	1 800	30 580	0.14	—	—	—	[64]
"	ethanol	35 210	1 480	29 411	0.10	2.7	32 062	0.90	[64]
N-Methylaniline	cyclohexane	33 900	—	—	—	—	—	—	[99]
NN-Dimethylaniline	"	33 444	—	—	—	—	—	—	[99]
β-Naphthylamine	"	—	5 600	—	0.33	6.9	—	—	[148]
"	ethanol	—	—	—	0.46	16.6	—	—	[148]
α-Naphthylamine	cyclohexane	31 250	2 000	26 670	0.46	6	—	—	[148]
"	ethanol	—	—	—	0.57	19.5	—	—	[148]
1-Aminoaphthalene-sulphonic acid	DMF	28 490	—	21 690	0.82	27.3	—	—	[148]
"	acetonitrile	20 070	—	21 690	0.82	28.5	—	—	[148]
"	methanol	29 325	—	20 620	0.24	17.3	—	—	[148]
1-Aminoanthracene	water–ethanol	—	4 000	—	—	—	21 650	—	[87]
2-Aminoanthracene	"	—	4 000	—	—	14	22 100	—	[87]
9-Aminoanthracene	"	—	4 000	—	—	—	21 500	—	[87]
2-Aminonaphthalene-1-sulphonic acid	methanol	29 000	—	25 060	0.39	4.46	—	—	[87]
Ditto	water	29 411	—	24 900	0.21	2.03	—	—	[87]
o-Aminobenzoic acid	cyclohexane	29 800	—	25 800	—	—	—	—	[151]
Ditto	benzene	29 600	—	25 200	—	—	—	—	[151]
"	ethanol	29 800	—	24 200	—	—	—	—	[151]
m-Aminobenzoic acid	cyclohexane	31 000	—	26 000	—	—	—	—	[151]
Ditto	ethanol	31 300	—	22 700	—	—	—	—	[151]
"	acetonitrile	31 000	—	24 600	—	—	—	—	[151]
p-Aminobenzoic acid	benzene	35 100	—	30 700	—	—	—	—	[151]
Ditto	ethanol	34 600	—	29 000	—	—	—	—	[151]
"	acetonitrile	35 100	—	29 900	—	—	—	—	[151]
Methyldiphenyl-amine	cyclohexane	34 245	12 500	—	0.042	—	24 600	0.89	[136]
Diphenylamine	"	35 460	17 400	—	0.05	3.2	25 200	0.38	[136]
Triphenylamine	"	33 333	23 700	—	0.072	—	24 500	0.88	[136]
"	toluene	—	—	—	0.045	—	—	1.05	[111]
1-(*NN*-Dimethylamino)-naphthalene	cyclohexane	31 850	—	26 320	0.011	0.13	—	—	[147]
"	acetonitrile	31 850	—	23 670	—	—	—	—	[147]
"	THF	32 050	—	24 540	0.12	1.58	—	—	[147]
2,2,4-Trimethyl-1,2-dihydroquinoline	cyclohexane	29 070	3 200	—	0.31	6.78	—	0.02	[123]
6-Ethoxy-DHQ	"	27 030	3 000	—	0.33	8.44	—	0.014	[123]
6-Hydroxy-DHQ	"	28 090	3 600	—	0.39	8.80	—	0.017	[123]
N-Acetoxy-2,2,4-trimethyldihydro-quinoline	"	32 258	5 000	—	—	—	—	—	[120]
2,2,4-Trimethyl-THQ	"	—	—	—	0.17	2.79	—	—	[53]
4-Phenyl-THQ	benzene	—	—	—	0.09	2.33	—	—	[53]
6-Aminochrysene	cyclohexane	29 600	21 880	25 100	0.28	—	—	—	[150]
"	ethanol	29 500	19 050	22 935	0.25	—	—	—	[150]
"	water	29 410	—	21 280	0.16	—	—	—	[150]

Notation: ν_{abs}, ϵ_{max}, and ν_{fl} are the long-wavelength maximum in the absorption spectrum, the extinction coefficient at the maximum, and the maximum in the fluorescence spectrum respectively, ϕ_{ISC} is the intersystem conversion quantum yield, and DHQ and THQ represent 1,2-dihydroquinoline and 1,2,3,4-tetrahydroquinoline respectively; for the significance of the remaining notation, see the footnote to Table 1.

In the S_1 state the principal properties of aniline are weakened and the anilinium ion dissociates adiabatically in the excited state at room temperature; the fluorescence of aniline itself is then observed.[69]

Aminoanthracenes and 1,2-dihydroquinolines in the excited state undergo acid dissociation: a longer-wavelength fluorescence band, corresponding to emission by the anthramide anion[87] or the corresponding anion derived from 1,2-dihydroquinolines,[88] appears in the spectrum in highly alkaline solutions.



Thus, a common feature of all aromatic amines is the weakening of the basic and intensification of the acid properties when they are excited to the S_1 state, which leads to the effective quenching of the fluorescence of amines by proton donors.[70–74]

The mechanism of the dissipation of the electronic excitation energy in the phototransfer of a proton has been studied in detail.[70–72] It has been shown in relation to aqueous and alcoholic solutions of β-naphthylamine, 3-aminopyrene, and 2-aminoanthracene that in highly acid solutions of the amines the excited states of the latter undergo effective induced deactivation by protons.[70,71] This process apparently involves the protonation of aromatic amines in the aromatic ring. At acid concentrations of 2–5 M, the appearance of a third emission band of amines (apart from the fluorescence bands of the neutral amine and the cation), which is due to the fluorescence of a carbonium ion, has been observed[71] in the range 550–580 nm. This means that the protonation process is adiabatic without loss of excitation.

The possibility of the induced deactivation by the proton of the excited states of 1- and 2-naphthylamines, formed as a result of the dissociation of their cations in the excited state, has also been noted[74] but it has been attributed to adiabatic deactivation.

The p*K* of the amines in the ground and excited states have been listed in another review[73] and will not be quoted here.

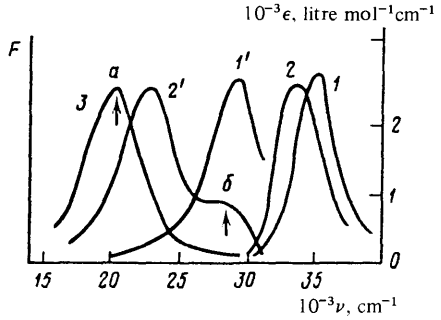


Figure 1. Absorption and fluorescence spectra of *p*-cyano-3-methyl-*NN*-dimethylaniline:[75,81] 1) and 1') in methylcyclohexane; 2) and 2') in dichloromethane; 3) in acetonitrile (the absorption spectrum in acetonitrile is close to that in methylcyclohexane and is not presented here).

(b) The luminescence properties of amine molecules with a "twisted intramolecular charge transfer state"

NN-Dialkyl-*p*-cyanoanilines (and in general anilines with electron-donating and electron-accepting substituents in the *para*-position) occupy a special place among aniline

derivatives.[62,75-86] A characteristic feature of these compounds is the two-component fluorescence of their solutions in polar solvents (Fig.1).[75] In a non-polar solvent (methylcyclohexane) there is only one "normal" fluorescence band of *NN*-dialkyl-*p*-cyanoanilines, while in more polar solvents there are two components *a* and *b*, the intensity and bathochromic shift of the long-wavelength component *a* increasing with solvent polarity.

Detailed studies of the luminescence,[76-78] luminescence spectroscopic,[79,80] and photochemical[85] properties of the above compounds led to the conclusion that a type of excited states (Fig.2), hitherto unknown, exists for these compounds—"states with twisted intramolecular charge transfer" (TICT) in the terminology adopted by Grabowski et al.[75] Quantum-chemical calculations showed that complete intramolecular charge transfer from the unshared electron pair of the $N(CH_3)_2$ group to the π^* orbital of the CN substituent[81] is possible for these compounds in the conformation where the angle α between the planes of the donor and acceptor is 90°.

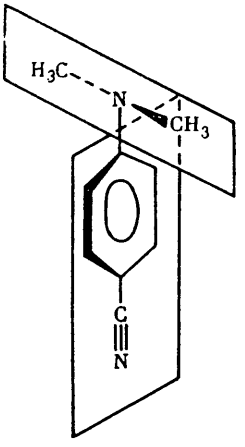
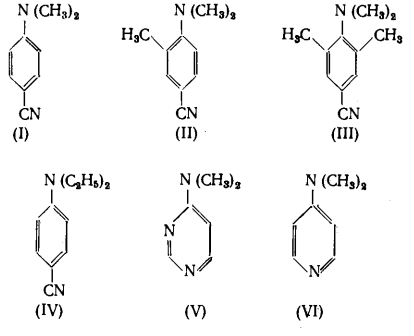
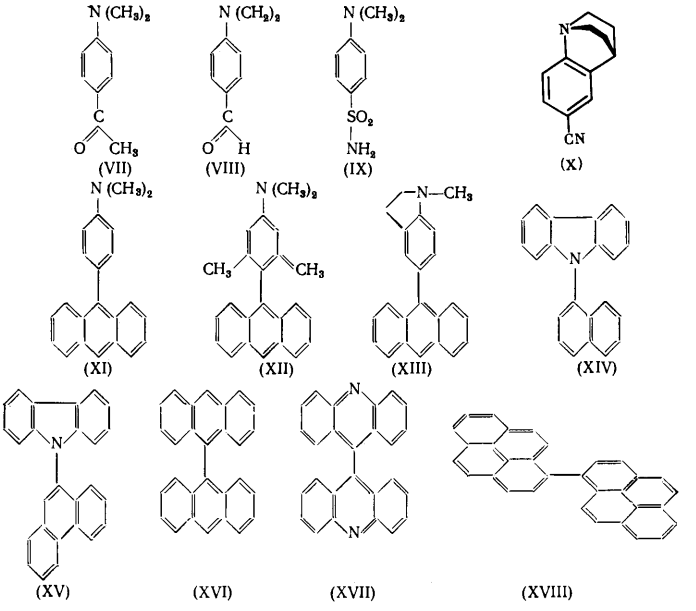


Figure 2. The "twisted state" of *p*-cyano-*NN*-dimethylaniline.

The formulae of all the compounds for which TICT has been postulated are given below.[75]





Thus, when *NN*-dialkyl-*p*-cyanoanilines are irradiated, the usual delocalised π,π^* state is initially excited, as in all other aniline derivatives. In non-polar solvents this state exhibits the usual fluorescence (the *b* band); but in polar solvents rapid $b^* \rightarrow a^*$ relaxation takes place and radiation is emitted from this TICT state (the *a* band). In solvents of moderate polarity the $b^* \rightleftarrows a^*$ equilibrium obtains and both fluorescence bands are shown.

The kinetics of the solvation by alcohol of the TICT state of *p*-dimethylaminobenzonitrile have been followed directly by the method of picosecond laser photolysis.[82] It follows from the results of these measurements that the equilibrium between the planar and TICT states in propanol is established after ~20 ps; the constant of this equilibrium has been estimated (not less than 30 in propanol and not less than 25 in butanol). A second value of the formation time of TICT state, amounting to 11 ps, has been determined from the kinetics of the quenching of the two-component fluorescence of *p*-dimethylaminobenzonitrile by oxygen[75,81] and, according to these data, the rate of formation of the TICT state does not depend significantly on the viscosity.

The most convincing proof of the role of the TICT states in the emission of the anomalous fluorescence band has been provided by structural studies.[75,81] The authors studied in detail the luminescence spectroscopic properties of various sterically hindered anilines and showed that, for compounds (II) and (III) whose *ortho*-positions relative to the amino-group contain methyl groups (in which the twisted structure is as it were "fixed"), only the *a* band is observed, while compound (I) emits both bands.

The fluorescence of compounds (I)–(III) in the TICT state must be rigorously prohibited both by steric factors (owing to the minimum overlap of the orbitals involved in the transition for the "twisted" conformation) and by the symmetry ($A_2 \leftarrow A_1$ transition in the C_{2v} point group). However, extremely low activation energies have been obtained from the temperature variation of the emission rate constant: $k_B = k_0 + k_1 \exp(-hcE/kT)$, $E \approx 120$–200 cm^{-1}. Such low values of E are associated with the occurrence of torsional vibrations, which increase the overlap between the donor and acceptor orbitals and thus increase the probability of the radiative transition.

The luminescence properties of *p*-dimethylaminobenzaldehyde (VII) and its derivatives (XVI) are even more complex.[77] Apart from the emission bands *a* and *b* associated with the TICT, the spectra of these compounds show bands due to aggregates and excimers.

In non-polar solvents the monomer of *p*-dimethylaminobenzaldehyde does not fluoresce at all in the lowest $S_1(n\pi^*)$ state and only phosphorescence in the $T_1(\pi,\pi^*)$ state is observed; in polar solvents a band *b* due to the fluorescence in the $S_1(\pi,\pi^*)$ state is observed. With increase of solvent polarity, there is a bathochromic shift of the band corresponding to the emission from the TICT state.

The fluorescence quantum yield of *p*-dimethylaminobenzaldehyde and *p*-dimethylaminoacetophenone in methyltetrahydrofuran depends on the excitation wavelength (Table 7).[84]

Table 7. The fluorescence (ϕ_{fl}) and phosphorescence (ϕ_{phosph}) quantum yields for *p*-dimethylaminobenzaldehyde (DAB) and *p*-dimethylaminoacetophenone (DAA).[84]

Amine	Solvent	φ_{fl}		φ_{phosph}
		λ_{exc} = 338 nm	λ_{exc} = 357 nm	
DAB	methyl-THF	—	0.09	0.20±0.015
DAB	propanol	0.56	0.93	0.07±0.017
DAB	methanol-water	0.98	—	0.014
DAA	methyl-THF	<0.01	—	0.44±0.05
DAA	propanol	0.32	—	0.04

The existence of several conformers of compounds (I) and (II) in the ground state follows from the discrepancy between the fluorescence excitation spectra of the two compounds and their absorption spectra. The fluorescence quantum yield of compounds (I) and (II) increases appreciably with decrease of temperature: at 77 K it is greater by two orders of magnitude than at room temperature, which is associated, according to the authors,[84] with the presence of conformers also in the TICT state, the relaxation of the initially populated planar state to form the TICT state being controlled by diffusion.

Calculations by the CNDO/S method have confirmed the existence of a whole series of conformers of compounds (I) in the ground and excited states, which are characterised by different angles of rotation of the $-N(CH_3)_2$ and $-CHO$ goups relative to the plane of the ring and by different degrees of hybridisation of the nitrogen atom, which is also responsible for the dependence of the fluorescence and phosphorescence spectra on the excitation wavelength.[86]

3. Photochemical Properties

The photochemical properties of aromatic amines are classified in this Section in terms of the type of the primary processes undergone by the amines. Four possible processes are examined: photodissociation of the N–H bond, photoionisation and formation of exciplexes, photodissociation of the C–N bond, and photorearrangements in the aromatic rings.

(a) Photodissociation of the N–H bond

Photoirradiation of solutions of primary and secondary aromatic amines in non-polar solvents leads to the rupture of the N–H bond and the formation of hydrogen atoms and aminyl radicals:

$$RNH + h\nu \rightarrow R\dot{N} + H \cdot$$

Aminyl radicals have been detected by flash photolysis in the photoirradiation of aniline and *N*-methylaniline,[89,94] 1,2-dihydroquinolines,[90–92] 1,2,3,4-tetrahydroquinolines (Fig. 3),[93] indoles,[94,96] 7-azaindolines,[97,98] and indolines.[100] The formation of hydrogen on photolysis of aniline and 1,2-dihydroquinolines has also been demonstrated mass-spectrometrically and chromatographically.[89,101]

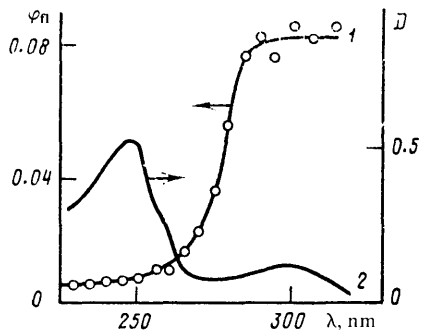


Figure 3. Dependence of the fluorescence quantum yield for a solution of 1,2,3,4- tetrahydroquinoline on the excitation wavelength (curve *1*) and the absorption spectrum of its solution in heptane (curve *2*).

The photodissociation quantum yields and the extinction coefficients of the aminyl radicals formed are presented in Table 8.

In non-polar solvents the neutral aminyl radicals are as a rule destroyed via a second order reaction in the absence of oxygen as a result of disproportionation or recombination:

$$2RN \rightarrow \text{products.}$$

The rate constants for this process are 1.5×10^9 litre $mol^{-1}s^{-1}$ for anilino-radicals in hexane[89] and 8.9×10^7 litre $mol^{-1}s^{-1}$ for 1,2-dihydroquinoline radicals.[101]

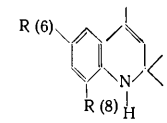
It has been shown[88,102] both experimentally and by quantum-chemical calculations that aminyl radicals are much stronger bases than the initial amines.

In aqueous and aqueous alcoholic solutions radical-cations are therefore formed in the photolysis of amines even at neutral pH:

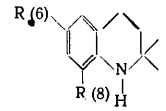
$$RNH + h\nu \rightarrow R\dot{N} + H \underset{-H^+}{\overset{+H^+}{\rightleftarrows}} RNH^+.$$

For example, the p*K* for the equilibrium $C_6H_5\dot{N}H + H^+ \rightleftarrows C_6H_5NH_2^+$ is 7.0 ± 0.1;[88] for 1,2-dihydroquinolines, the p*K*

are as a rule higher (Table 9).



(XIX): R (6)=R (8)=H
(XX): R (6)=H, R (8)=OH
(XXI): R (6)=CH_3, R (8)=H
(XXII): R (6)=H, R (8)=CH_3



(XXIII): R (6)=R (8)=H
(XXIV): R (6)=OH, R (8)=H

Table 8. The quantum yields in the photodissociation of the N–H bond and the extinction coefficients of the aminyl radicals formed.

Amine	Solvent	Radical		λ_{exc}, nm	Φ	Refs.
		λ_{max}, nm	ϵ, litre $mol^{-1}s^{-1}$			
Aniline	cyclohexane	400	670*	276	10^{-3}	[89]
"	"	308	4700**	254	0.07±0.02	[99]
N-Methylaniline	"	314	—	—	—	—
"	"	400	—	254	0.0054	[99]
Phenylethylamine	"	—	—	254	0.01	[99]
"	"	—	—	214	0.045	[99]
2,2,4-Trimethyl-1,2-dihydroquinoline	benzene	420	7500**	340—360	0.011	[123]
"	"	—	—	200—280	0.030	[123]
6-Hydroxy-DHQ	"	—	—	200—280	0.42	[123]
6-Methyl-DHQ	"	400	5000**	200—280	0.016	[123]
8-Methyl-DHQ	"	400	3000**	200—280	0.17	[123]
"	"	—	—	340—360	0.012	[123]
4-Methyl-7-azaindoline	hexane	400	457***	340—360	0.24	[97]
4,6-Dimethyl-7-azaindoline	hexane	400	457***	340—360	0.36	[97]
4,6-Dichloro-7-azaindoline	hexane	400	457***	340—360	0.22	[97]

*The extinction coefficient was determined by comparison with the spectrum of stable 2,4,6-di-t-butylanilino-radical.
**The extinction coefficient was determined by the simultaneous measurement of the absorption spectra of the anilino-radicals at 77 K in 3-methylpentane and the determination of the amount of radicals in this spectrum with the aid of EPR spectra.[123]
***The extinction coefficient was determined by the method of Malkin et al.[98] involving the comparison of the amount of aminyl radicals formed in the direct and benzophenone-sensitised photolysis.

The aniline radical-cations formed on photolysis are destroyed in water via a second-order reaction with a rate constant of 1.5×10^9 litre $mol^{-1}s^{-1}$ apparently as a result of the formation of dimeric complexes.[89]

So far little is known about the mechanism of the photodissociation of aromatic amines, particularly about the nature of the electronically excited state in which photodissociation takes place. The main source of the difficulty in determining the mechanism is the lack of quantitative information about the efficiency of the photodissociation due to the complexity of the quantitative determination of the aminyl radicals and hydrogen atoms formed on photolysis of amines.

The nature of the photochemically active excited state in such reactions was investigated for the first time only recently: for anilines, 1,2-dihydroquinolines, and 1,2,3,4-tetrahydroquinolines, we observed[90,93,99] the dependence of the fluorescence (Fig. 4) and photodissociation quantum yields on the excitation wavelength, which permitted the conclusion that, on excitation at the wavelength corresponding to the long-wavelength band in the absorption spectrum, the photodissociation takes place in the lowest singlet state (the lowest triplet state for tetrahydroquinolines) and that, with increase of the excitation energy, a new photodissociation channel is opened—via the highest excited states.

Table 9. The excess electron density at the nitrogen atom in the amine or in the aminyl radical (q_N) and the pK of the radical-cation (according to Pirogov and Malkin.[88,102]

Amine	q_N		pK	
	molecule	radical	molecule	radical*
(XIX)	−0.2089	−0.2141	4.7	10.8
(XX)	−0.2021	−0.2026	4.8	—
(XXI)	−0.2087	−0.2156	3.6	10.3
(XXII)	—	—	3.7	9.4
(XXIII)	−0.2140	−0.2091	4.55	13.0
(XXIV)	−0.2101	−0.1992	4.8	—
Aniline	—	—	4.58	7.0

*The pK were determined in an aqueous solution of ethanol at the point where the absorption spectrum of the neutral radical appeared.

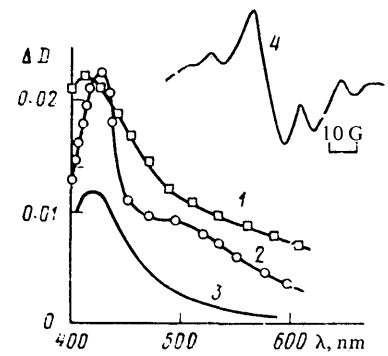


Figure 4. Absorption spectra of heptane solutions of the short-lived intermediates formed on photolysis of 1,2,3,4-tetrahydroquinoline [1) compound (XIX); 2) compound (XX)] and the absorption (curve 3) and EPR (curve 4) spectra of the aminyl radicals formed on photolysis of compounds (XIX) in vitreous 3-methylpentane matrix at 77 K.

The yield in the photochemical decomposition of aniline on photoexcitation with light at $\lambda = 254$ nm is 0.1, which is close to the quantum yield in the evolution of H_2. This shows that processes other than the dissociation of the N–H bond hardly occur in the photolysis of aniline in cyclohexane.[99]

At the present time the only question that remain obscure is whether the dissociation of the N–H bond in the highest excited states is responsible for the observed dependence on wavelength of the fluorescence quantum yields of aniline and other amines. Evidently, other photochemical processes (for example, reversible photoisomerisation of the benzene ring with formation of Dewar benzene) cannot induce this

process, because the fluorescence quantum yield of *NN*-dimethylaniline is almost independent of the excitation wavelength.[99] The dependence of the fluorescence and photochemical decomposition quantum yields of anilines and hydrogenated quinolines on the excitation wavelength is observed only in non-polar solvents and in water, while in alcohol there is no such dependence, which is apparently due to the recently observed formation of complexes between amines and alcohols.[103]

According to Köhler and Getoff[99] and Robin,[104] many amines exhibit low-lying Rydberg $n,3s$ states in the region of 40000 cm^{-1}. It appears probable that on excitation to the S_2 state, aniline (an in general all primary and secondary amines) undergo a transition onto the Rydberg potential surface, where bond dissociation takes place. A calculation[105] of the energies of the excited states of 1,2-dihydroquinolines by the CNDO/S method taking into account 40 excited configurations showed that a sharp increase of the photodissociation quantum yield takes place in the region of the $T_8(\sigma,\pi^*)$ state localised at the NH fragment (Fig.5).

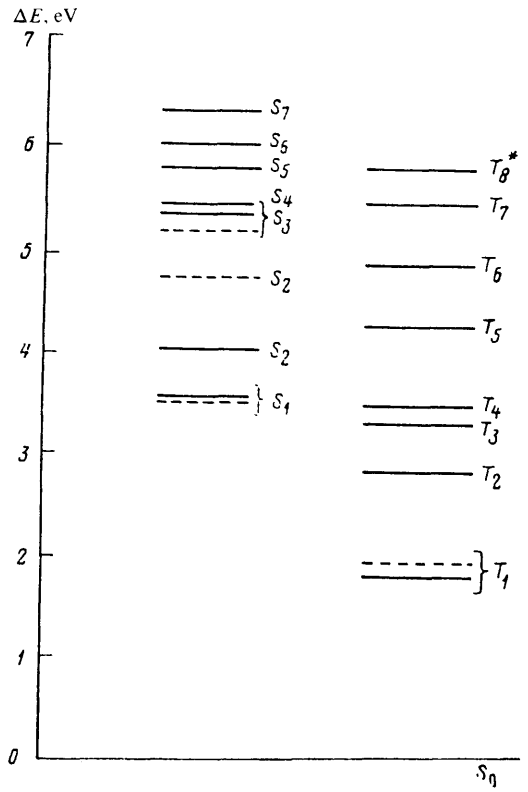


Figure 5. Energy level diagram for the electronically excited states of 2,2,4-trimethyl-1,2-dihydroquinoline (continuous line—calculation; dashed line—experiment). The σ,π^* states are marked by an asterisk; the others are π,π^* states.

The calculation demonstrated that all the electronically excited states of dihydroquinolines with energies less than 56000 cm^{-1} are delocalised over the entire molecule. The question therefore arises in what way the excitation energy of the entire π-system leads to the dissociation of the N–H bond.

There exist two different mechanisms of such a process which can be achieved, in principle, for the molecules of aromatic amines:[106,107] photodissociation in a bound state (adiabatic photodissociation) and predissociation. In the former case the electronic excitation energy, delocalised over the entire molecule, is converted into the vibrational energy of an individual N–H bond, while in the latter case it is converted into the electron ic energy of this bond. Convincing evidence for the particular photodissociation pathway in the condensed phase is at present lacking for any complex molecules (with the exception of the photodissociation of triphenylmethane[107]). For dihydroquinoline molecules, one can postulate that, when the excitation energies are below 42000 cm^{-1}, the N–H bond dissociates in a bound state via a non-adiabatic mechanism (Fig.6). Since the N–H bond dissociation energy is 3.46 eV (27890 cm^{-1}) (aniline), the rate of photodissociation via the adiabatic mechanism should be fairly low (the rate constant for the photodissociation of a C–H bond with the same strength by radiation with an energy of 54000 cm^{-1} does not exceed 10^6),[106] which is confirmed by the low dissociation yield on excitation at the wavelength corresponding to the long-wavelength absorption band (Table 10).

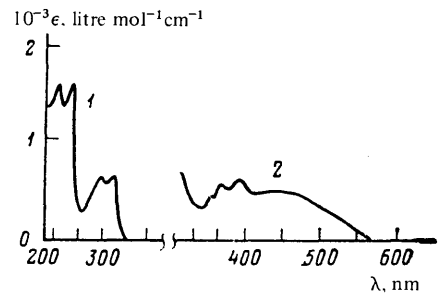


Figure 6. Absorption spectra of 1-cyano-2-hydroxy-1,2-dihydroquinoline in EPA at 77 K: 1) before irradiation with ultraviolet light; 2) after irradiation with ultraviolet light.

Table 10. The ionisation energies in vacuo (I_g) of the commonest amines.

Amine	I_g, eV	Refs.
Triphenylamine	6.68	[4]
Diphenylamine	7.25	[4]
Tetramethylphenylenediamine	6.2	[4]
Aniline	6.60	[4]
Indole	7.44	[6]
Carbazole	7.20	[151]

When the excitation energy exceeds 42000 cm^{-1}, the transition of the molecule to the repulsion state of the N–H bond and the occurrence of photodissociation via the predissociation mechanism become possible. It has been shown[106] that the repulsion state of the C–H bond (and in general the

R–H bond) is of the triplet type, i.e. the dissociation of the N–H bond can take place with an appreciable yield only in the triplet state.

Thus, for low excitation energies (less than 42000 cm^{-1}), the photodissociation of the N–H bond proceeds via the adiabatic mechanism with a low quantum yield (<0.01). When the energies are in excess of 42000 cm^{-1}, a new channel appears, leading to the dissociation of the N–H bond via predissociation, which increases the efficiency of the overall process. The nature of the increased quantum yield in the dissociation of the N–H and O–H bonds in the photoirradiation of indoles and phenols observed in a series of studies,[94,95,99,109] which involves the operation of two photodissociation mechanisms, is analogous.

(b) Photoionisation

By photoionisation we understand the direct transfer of an electron under the influence of light to the condensed phase with formation of a solvated electron.[4] Photoionisation is characteristic of compounds with a low ionisation potential (*p*-phenylenediamine and its methyl derivatives), while photodissociation predominates for amines with a relatively high ionisation potential (virtually all the remaining amines). The ionisation energy threshold J is defined by the expression

$$J = J_g - P_+ - V_0,$$

where J_g is the ionisation energy in the gas, P_+ the energy of the ionisation of the medium by the cation (radical-cation), and V_0 the energy of the interaction of the excess electron with the medium.

It follows from the data in Table 10 that the photoionisation of aromatic amines in the liquid phase can proceed via both one-quantum and two-quantum mechanisms. In non-polar solvents the differences between the energies of the one-quantum photoionisation of tetramethylphenylenediamine (TMPD) are determined by the quantity V_0 (V_0 for non-polar liquids varies from +0.6 eV for tetramethylsilane to −0.1 eV for n-hexane),[4–6] while the absolute value of the photoionisation threshold of TMPD is in the range from 4.3 eV in tetramethylsilane to 4.99 eV in n-hexane.[4] On photoexcitation of aromatic amines in non-polar solvents (other than TMPD) at the wavelength corresponding to the long-wavelength absorption band, photoionisation should therefore proceed extremely ineffectively.

It has been recently observed[113] that the photoionisation of TMPD on irradiation with light having energies in the range 42000–62000 cm^{-1} in weakly polar solvents (tetramethylsilane, 2,2-dimethylbutane, isoctane, cyclohexane, and n-hexane) leads to the formation of an electron–cation geminal ion pair, which either dissociates into the free ions or (with a significantly higher proabability) recombines to form excited TMPD, which emits recombination fluorescence.

In polar solvents the photoionisation is in general much more effective. The photoionisation of 2,7-bis(dimethylamino)-4,5,9,10-dihydropyrene in acetonitrile takes place in the fluorescent S_1 state, which is destroyed with formation of a radical-ion pair comprising the radical-cation of the amine and the radical-anion of acetonitrile; this pair subsequently dissociates into the free radical-ions (after 9 ns).[114] In benzonitrile the same compound forms an exciplex with the solvent and in this case the ionic photodissociation takes place directly in the exciplex.[115]

On the other hand, it has been shown[116] that the one-quantum ionisation of 1,6-bis(*NN*-dimethylamine)pyrene in acetonitrile proceeds via the intermediate formation of a long-lived (several microseconds) ion pair comprising the amine radical-cation and the solvated electron, which subsequently dissociates into the free ions.

In a detailed study[117] it was observed that the photodissociation of *NNN'N'*-tetramethylbenzidine (TMB) in acetonitrile, benzonitrile, and pyridine proceeds via an exciplex with the solvent, from which a radical-ion pair is formed (in the case of acetonitrile this ion pair comprises the amine radical-cation and the radical-anion derived from the acetonitrile dimer) and, in contrast to the ion pairs formed by 2,7-bis(*NN*-dimethylamine)-4,5,9,10-dihydropyrene, this ion pair is so long-lived that before dissociation it has sufficient time to react with acetonitrile to form the polymeric ion pair $TMB^+...(CH_3CN)^-$. Thus the formation of exciplexes with the solvent is a fairly general mechanism of the one-quantum photoionisation of aromatic amines in polar solvents such as acetonitrile, benzonitrile, dimethylformamide, and pyridine.

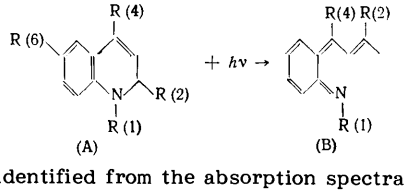
(c) Dissociation of the C–N bond in aromatic amines

In contrast to aliphatic amines, where the dissociation of the C–N bond takes place fairly frequently and has been reliably identified, there is very little reliable evidence for the dissociation of the C–N bond in aromatic amines. It has been observed[118] by EPR that the photoirradiation of TMPD in perdeuterio-3-methylpentane at 77 K leads to the formation of only one product, namely the methyl radical, as a result of the two-quantum C–N bond dissociation reaction in TMPD.

It has been demonstrated spectrophotometrically[119] that ultraviolet irradiation of frozen solutions of *NN*-dimethylaniline in EPA and 3-methylpentane at 77 K results in the formation of the anilino-radical $C_6H_5\dot{N}CH_3$ (the maxima in the absorption spectrum are at 314.0 and 400.0 nm). These bands usually overlap with the absorption bands of the dimethylaniline radical-cation. However, infrared irradiation of a solution subjected to preliminary irradiation with ultraviolet light at 77 K makes it possible to eliminate the radical-cations (as a consequence of the liberation of solvated electrons from traps and their recombination with the radical-cations) and to obtain the absorption spectrum of the anilino-radical. Thus the homolytic photodissociation of the C–N bond has been suggested as the primary photochemical reaction of *NN*-dimethylaniline.

The dissociation of the C–N bond with formation of the anilino-radical is possible also in the liquid phase;[89] thus anilino-radicals appear in the photolysis of *NN*-dimethylaniline in benzene, although the probability of this process is much less than the probability of the dissociation of the N–H bond.[89]

The photodissociation of the C–N bond has been studied in greatest detail in aromatic amines in relation to the opening of the ring of 1,2-dihydroquinolines.[120–126] The photoirradiation of solutions of 1,2-dihydroquinolines in EPA at 77 K entails the ruputre of the C–N bond and the formation of brightly coloured products with a quinonaldine structure:



(A) (B)

which were identified from the absorption spectra (Fig.6). The reverse thermal reaction takes place in the dark.

The mechanism of the formation of the quinonaldine form is apparently analogous to the mechanism of the opening of the pyran ring in pyrans, chromenes, and spiropyrans,[127–129] i.e. the excitation involves the ruputre of the C–N bond, a change in the hybridisation of the nitrogen atom, and the

rotation of both parts of the molecule about the C(3)–C(4) bond with formation of an almost planar quinonaldine structure. The probability of the dissociation of the C–N bond is determined by the nature of the substituents in the R(1) and R(2) positions and occurs only for dihydroquinolines with electron-accepting groups at the nitrogen atom.

In vitreous solutions at 77 K all the dihydroquinolines are photochemically stable. It has been observed[122] that the opening of the ring in dihydroquinolines is sensitised by triplet energy donors, which proceeds via the lowest state $T_1(\pi,\pi^*)$ having a closed or cyclic form. In contrast to the photochromic chromenes and spiropyrans, there exist no quantitative data concerning the effectiveness of the opening of the ring in dihydroquinolines on irradiation with ultraviolet light.

It is noteworthy that dihydroquinolines containing only a hydrogen atom as the substituent at the nitrogen do not undergo the ring opening reaction on photoirradiation and only the dissociation of the N–H bond takes place.[120,121] The energy level diagrams for the initial compound and the products of the N–H and C–N bond dissociation reactions of dihydroquinolines have been constructed on the basis of quantum-chemical calculations by the PPP method[126] and have made it possible to put forward the following reaction scheme:

$$(A) \xrightarrow{h\nu} (A(S_1)) \rightarrow (A(T_1)) \begin{cases} \rightarrow (B(T_1)) \rightarrow (B(S_0)); \\ \rightarrow R\dot{N}(S_0). \end{cases}$$

Calculations of the transition energies, atomic charges, and Viberg indices for the lowest singlet and triplet transitions of the *N*-acyl-substituted and unsubstituted dihydroquinolines have shown that an electron-accepting substituent at the nitrogen atom weakens the C–N bond; the photoexcitation of dihydroquinoline molecules leads to the same effect. For dihydroquinolines without substituents at the nitrogen atom, a new channel leading to the degradation of the excitation energy appears, namely the dissociation of the N–H bond, which occurs much more effectively than the dissociation of the C–N bond.

The luminescence properties of 1,2-dihydroquinolines and 1,2,3,4-tetrahydroquinolines containing hydrogen as the substituent at the nitrogen atom have been investigated in detail.[129–135] It has been observed that the first and second absorption bands in the spectra of dihydroquinolines shift in different directions under the influence of the solvent,[133] which indicates their different nature.

It has been shown by infrared spectroscopy that di- and tetra-hydroquinolines form complexes with chlorine-containing solvents in the ground state. In aqueous alcoholic solutions bands due to the $T_1 \leftarrow S_0$ transitions are observed after the introduction of KI.[129] The energies of the T_1 states of dihydroquinolines determined from these spectra are consistent with the values obtained from the phosphorescence spectra.[123]

4. Photorearrangements

The most important and most thoroughly investigated reaction of aromatic amines, which involves the benzene ring, is the photocyclisation of diphenylamines to carbazoles.[136–142]

It is known that the photoirradiation of derivatives of diphenylamine leads to the almost quantitative formation of carbazoles in almost all solvents (Fig.7).[136–138]

It follows from the experiments on the quenching of fluorescence and the sensitisation of the photocyclisation of diphenylamine and triphenylamine in hexane that the cyclisation takes place in the T_1 states of the amines via the intermediate formation of a short-lived product (E) (Table 11). Carbazole is formed from (E) as a result of the thermal elimination of two hydrogen atoms (it has been specially demonstrated that the amount of H_2 evolved is consistent with the amount of carbazole formed[139]).

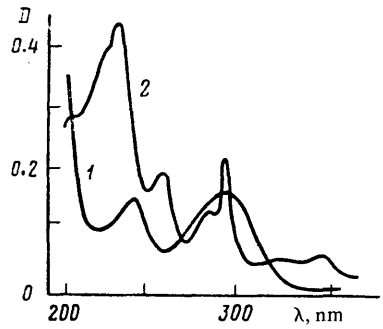


Figure 7. The conversion of *N*-methyldiphenylamine into carbazole: 1) absorption spectrum of a 2.6×10^{-5} M solution in hexane before irradiation; 2) after irradiation with ultraviolet light.

Table 11. The quantum yields in the formation of carbazole (ϕ_1) and the consumption of diphenylamine (ϕ_2) on irradiation with light at $\lambda = 253.7$ nm.[138,139]

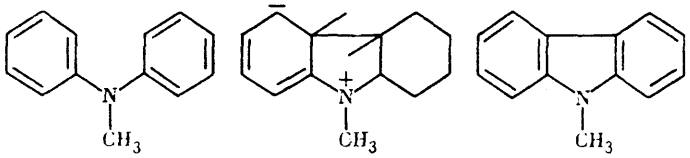
Solvent	Presence of oxygen*	φ_1	φ_2
Methyldiphenylamine			
Cyclohexane	+	0.67	0.67
Cyclohexane	—	0.06	0.06
Methylcyclohexane	+	0.67	0.67
Methylcyclohexane	—	0.06	—
n-Hexane	+	0.62	0.62
n-Hexane	—	0.06	—
Ethanol	+	0.57	—
Diphenylamine			
Cyclohexane	+	0.06	0.07
Cyclohexane	—	0.10	—
Methylcyclohexane	+	0.06	—
n-Hexane	—	0.05	—
Ethanol	—	0.10	—
Triphenylamine			
Cyclohexane	+	0.12	0.12
Cyclohexane	—	0.003	—

*The "+" and "–" signs correspond to the presence and absence of oxygen respectively.

The appreciable increase of the quantum yield of the reaction in the presence of oxygen is due to the fact that the latter appreciably accelerates the elimination of hydrogen from (E) with formation of HO_2 or H_2O_2.

The lifetimes of the T_1 state of *N*-methyldiphenylamine and triphenylamine in cyclohexane at 20 °C have been determined as respectively 1.36×10^{-8} and 8.16×10^{-8} s.[139] It has been demonstrated directly by flash photolysis[141] that *N*-methyl-4*a*,4*b*-dihydrocarbazole (D) is formed directly from *N*-methyldiphenylamine in the T_1 state and that its spectrum has an absorption maximum at 610 nm. Compound (E) is then

converted into the carbazole (P) via the elimination of a hydrogen atom.



(D) (E) (P)

The quantum yields of 4*a*,4*b*-hydrocarbazole formed from *N*-methyldiphenylamine in the T_1 state have been estimated from the dependence of the yield of carbazole and *N*-methyl-4*a*,4*b*-hydrocarbazole on the oxygen concentration on irradiation by a flash or continuously; the yields are 0.89, i.e. the T_1 state is deactivated almost exclusively via conversion into compound (E).[142]

The unusual influence of oxygen on the yield of carbazole (the dependence of the yield on the oxygen concentration passes through a maximum at O_2 concentrations of 6×10^{-4} M for *N*-methyldiphenylamine and 2×10^{-5} M for diphenylamine in hexane) is associated with the dual role of oxygen: on the one hand, it deactivates the T_1 state of diphenylamines and, on the other, it accelerates the conversion of 4*a*,4*b*-dihydrocarbazoles into carbazoles.[142]

Complete quantitative information concerning the pathways leading to the dissipation of the electronic excitation energy has been obtained for a solution of *N*-methyldiphenylamine in cyclohexane at 20 °C,[141,142] fully confirming the proposed mechanism of the conversion of diphenylamines into carbazoles via the intermediate (E).

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The photonics of amine solutions possess in broad outline features characteristic of both aromatic and aliphatic amines, which makes it possible (despite the wide variety of structures and photochemical properties) to consider them within the framework of a single class of compounds. For all the amines in the lowest electronically excited states, the molecular geometry rearranges and undergoes a change in its electronic configuration, the two processes being associated with the intramolecular charge transfer on excitation and (or) the inclusion of the Rydberg states of the RN< fragment. This leads to an appreciable Stokes band shift in the fluorescence spectra in polar solvents, which is characteristic to a greater or lesser extent of all amines, starting from the simplest aliphatic amines and extending to indole. The main photochemical process for amines is electron transfer and the photodissociation of the N–H bond. The homolytic photodissociation of the N–H bond is the dominant process for all the primary and secondary amines in the absence of special conditions for electron transfer (polar solvents and electron acceptors).

It is essential to note that, whereas the luminescence spectroscopic properties of amines in the condensed phase have been investigated in fair detail and a fairly elegant theory, relating the electronic structure of amines to their luminescence spectroscopic properties has been constructed, the mechanism of the photochemical reactions of the same amines has been studied quite inadequately. The lack of quantitative data concerning the efficiency of N–H bond dissociation process makes it impossible to characterise the influence of the structure of the molecule on the mechanism of its photochemical reactions. This is why most difficulties are observed in the study of the many processes occurring when amine molecules absorb light in those cases where photodissociation processes are possible.

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The Chemiluminescence of Organometallic Compounds

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Studies on the liquid-phase and gas-phase reactions of organometallic compounds accompanied by the emission of light are described systematically and discussed. The influence of the magnetic field on the chemiluminescence of Grignard reagents and the study of the electrochemiluminescence of solutions of organometallic compounds are examined. The ways leading to further development of the field of the chemiluminescence of organometallic compounds and certain possible applications of the phenomenon in the monitoring of industrial processes are discussed.
The bibliography includes 80 references.

CONTENTS

I. Introduction 1058
II. The chemiluminescence of organolithium, organosodium, and organopotassium compounds 1058
III. The chemiluminescence of solutions of organomagnesium and organocalcium compounds 1059
IV. The chemiluminescence of solutions of organoaluminium compounds and the electrochemiluminescence of a rhenium carbonyl solution 1063
V. The chemiluminescence of organometallic compounds in the gas phase 1068
VI. Conclusion 1071

I. INTRODUCTION

As a phenomenon and as a specific method, capable of yielding much information, for the investigation of the mechanisms of chemical reactions, chemiluminescence (CL) has attracted the attention of investigators in increasing numbers of fields of research. The results of studies of the chemiluminescence excited in the reactions of organic[1-4] and inorganic[5] substances have been fairly fully described in a series of special reviews and have been used to investigate the kinetics of chemical reactions,[6,7] for the analytical determination of submicroamounts of substances in solution,[5,8] and also for the elucidation of the mechanism of the transformation of the energy of chemical reactions into the energy of electronically and vibrationally excited molecules.[9] On the other hand, there have been no reviews giving a systematic account of studies of chemiluminescence involving organometallic compounds (OMC) and only isolated data are available.[10,13]

Despite the fact that the emission of light in chemical reactions involving OMC was observed more than 70 years ago,[11,12] the study of the chemiluminescence of OMC has not been developed as much as it deserves. Nevertheless, the exceptionally extensive applications of OMC involving the large-scale manufacture of various organic products,[13,14] the preparation of specially pure metals,[15] and the creation of the laser technology[16] have made it necessary to resort to physicochemical methods for the investigation of the mechanisms of the reactions of OMC. The employment for this purpose of the chemiluminescence method is especially attractive, because it is possible to record the excited states of the reaction products and intermediates (here and henceforth, unless otherwise stipulated, electronically excited states are considered) without interfering with the system incorporating chemically corrosive OMC. The potential possibility of generating chemiluminescence in the redox reactions of OMC arises from their high rates and exothermic nature. Such reactions frequently constitute the basis of organic catalytic and non-catalytic synthesis. It has been noted[17] that most of the catalytic reactions proceed via the formation of excited states of unstable intermediates. Evidently the search for new chemical reactions involving OMC accompanied by chemiluminescence will make it possible to detect such excited states from their radiative deactivation.

The studies considered in this review have been subdivided in terms of the Groups of the elements in the Periodic System and are concerned with the chemiluminescence in solution and in the gas phase. The ability of many OMC to glow in air is generally known; since the emission of light observed under these conditions includes an equilibrium component, i.e. a glow unrelated to the phenomenon of chemiluminescence, this type of light emission is not considered in this review.

II. THE CHEMILUMINESCENCE OF ORGANOLITHIUM, ORGANOSODIUM, AND ORGANOPOTASSIUM COMPOUNDS

1. The Oxidation of Organolithium, Organosodium, and Organopotassium Compounds by Oxygen

Chemiluminescence in the oxidation of an ethereal solution of C_6H_5Li has been observed by Gilman et al.[18] A glow has also been detected in the analogous reactions of solid specimens of C_6H_5Li, C_6H_5Na, and C_6H_5K.[19] The chemiluminescence spectrum in the interaction of C_6H_5Li with a saturated solution of oxygen in benzene consists of a broad band (from 320 to 600 nm) with maxima at 350 and 530 nm.[20] Even at a low concentration of butyl-lithium (10^{-3} M) the solutions have a deep brown colour, which leads to a marked distortion of the chemiluminescence spectrum as a consequence of the self-absorption by the solution.

2. The Oxidation of Butyl-Lithium by Organic Peroxides

The emission of light in the oxidation of C_4H_9Li by benzoyl peroxide (BP), lauryl peroxide, and t-butyl peroxide in toluene, heptane, and tetrahydrofuran (THF) has been investigated.[21] Two sections, which can be expressed in a linear form in terms of the variables as a second-order kinetic equation, have been differentiated in the kinetic plot of the chemiluminescence intensity in the reaction of C_4H_9Li with BP (Fig.1):

$$I^{-1/2} = (k\eta)^{-1/2}[BP]_0^{-1/2} + (k/\eta)^{1/2}\, t,$$

where k is the reaction rate constant, η the chemiluminescence yield, and $[BP]_0$ the initial BP concentration. The

rate constant k obtained from chemiluminescence measurements[20] and the results of the iodometric titration of BP agreed satisfactorily (0.3 and 0.34 litre mol^{-1} s^{-1} respectively). The chemiluminescence yield η was 10^{-12} photons per single step in the interaction of the reactants. The effective activation energy was obtained from the temperature dependence of I (on the basis of the chemiluminescence kinetics) and is 3.0 ± 0.5 kcal mol^{-1}.

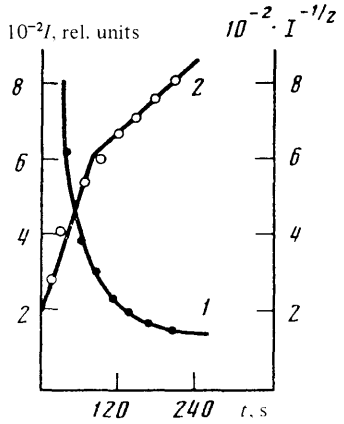
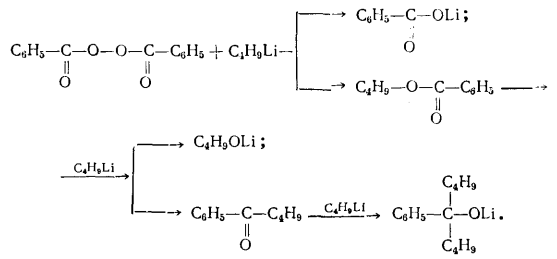


Figure 1. Kinetic curve describing the decrease of the chemiluminescence intensity (curve *1*) and its form in terms of the variables of Eqn.(1) (curve *2*);[21] $[BP]_0 = [C_4H_9Li]_0 = 10^{-2}$ M.

According to the results of the infrared spectroscopic and ^1H NMR analysis of the reaction products and the study of the stoichiometry of the interaction,[21] the mechanism of the complex process involving the oxidation of butyl-lithium by BP can be represented by the following consecutive reactions:



It is assumed that the source of excitation energy is the first, most exothermic stage (90–90 kcal mol^{-1}) [sic] and Panasenko et al.[21] believe that the chemiluminescence emitter is butyl phenyl ketone—the product of the second stage. The difference between the chemiluminescence and photoluminescence spectra of the suggested emitter (Fig. 2) is associated with the formation of its complex with another reaction product—lithium butoxide. Indeed, the photoluminescence spectrum of a mixture of chemically non-interacting acetophenone and lithium butoxide agrees with the short-wavelength chemiluminescence maximum (460 nm);[21] the nature of the second, long-wavelength chemiluminescence maximum has remained unelucidated. Thus the excitation of the chemiluminescence emitter occurs as a result of the transfer of the energy of the first stage of the process to butyl phenyl ketone—the product of the second stage. A more clear-cut argument in support of the proposed mechanism of the excitation of the chemiluminescence would have been the detection of an increase in chemiluminescence intensity when butyl phenyl ketone is added to the solution.

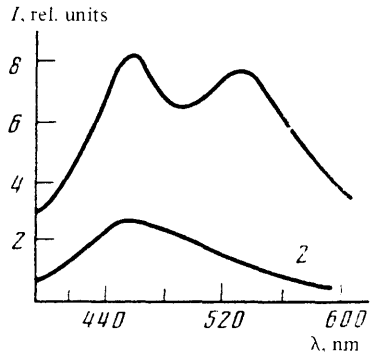


Figure 2. The chemiluminescence spectrum in the reaction of benzoyl peroxide with C_4H_9Li (curve *1*) and the photoluminescence spectrum of a mixture of acetophenone and C_4H_9OLi in heptane (curve *2*); 20 °C; $[BP] = [C_4H_9Li] = 10^{-2}$ M.

III. THE CHEMILUMINESCENCE OF SOLUTIONS OF ORGANOMAGNESIUM AND ORGANOCALCIUM COMPOUNDS

In 1905 Wedekind[22] attempted to obtain nitrotriphenylmethane by the reaction

$$3C_6H_5MgI + Cl_3CNO_2 \rightarrow (C_6H_5)_3CNO_2 + 3MgICl.$$

Although the desired product was not obtained, Wedekind observed a bright chemiluminescence arising when chloropicrin was added to a solution of the Grignard reagent (GR) in ether; the colour of the glow varied from yellow-green to pure green. In a number of his studies of this chemiluminescence, a glow was also detected in the reaction with phenylmagnesium bromide.[11,12,22] He attributed the observed glow to the phenomenon of luminescence (i.e. to a non-equilibrium emission of light), since the temperature of the system did not exceed the boiling point of ether. This first reaction of OMC accompanied by chemiluminescence was called the "Wedekind reaction". We may note that another communication by Wedekind[23] is referred in the literature to the same series of investigations, although it contains no information about chemiluminescence.

Later it was shown that a similar chemiluminescence arises in the interaction of chloropicrin and bromopicrin also with other Grignard reagents;[24] chloropicrin gave rise to a brighter glow. The iodides of Grignard reagents reacted with chloropicrin with emission of a greater amount of light than in the reaction of the chlorides. The mechanism of the chemiluminescence in the Wedekind reaction has still not been investigated. There is only no doubt that the reaction is different from that associated with the glow arising in the oxidation of Grignard reagents by oxygen, because it was observed in diethyl ether also under conditions where oxygen had been thoroughly removed.[25]

1. The Oxidation of Grignard Reagents by Oxygen

On repeating Wedekind's experiments, Heczko[26] observed the emission of light in the oxidation of Grignard reagents by oxygen. (Sometimes[27] the discovery of this chemiluminescence is erroneously attributed to Wedekind.[12]) It was assumed that the appearance of this glow requires moisture but later it was found[24,28] that the presence of moisture inhibits the glow. Subsequent investigations demonstrated that the chemiluminescence associated with the oxidation by oxygen is observed for a whole series of other Grignard reagents having different structures.[29–38] The glow in the oxidation of p-chlorophenylmagnesium bromide[30] is apparently one of the brightest among all the known chemiluminescence reactions in solution. This chemiluminescence, observed independently by Moeller[28] and Evans and Dufford,[32] has been called[24] the Moeller–Evans reaction.

There have been contradictory views concerning the influence of the nature of the Grignard reagent on its capacity for chemiluminescence and oxidation by oxygen. Moeller[28] assumed that this property is characteristic only of aromatic derivatives. According to Lifshitz,[31] the chemiluminescence is associated with the different stabilities of the etherates of aromatic and aliphatic Grignard reagents, because it has been found that all the ether-free Grignard reagents react with oxygen with emission of light; the brightness of the glow in the reactions of aromatic Grignard reagents is only a little lower than that of aromatic compounds. A systematic investigation[32] has shown that the above contradictions were associated with the influence of Grignard reagent concentrations, the optimum value of which (for the observation of the maximum brightness of the chemiluminescence) depends on their nature. Thus the concentration is 2.5 M for phenylmagnesium bromide and 0.33 M for aliphatic linear reagents such as propyl-, butyl-, and ethyl-magnesium bromides; at a concentration of 1 M chemiluminescence is not observed at all for these compounds. Apparently the author[31] dealt with less pure compounds in experiments involving the oxidation of concentrated solutions of aliphatic Grignard reagents.

Despite the lack of spectroscopic techniques available to modern investigators, the chemiluminescence intensities of various Grignard reagents observed in the old investigations (up to 1933) were compared on a quantitative basis using calibrated pyrometers. The spectroscopic characteristics of the glow were obtained either by visual observations or by a photographic procedure. This established many characteristic features of the appearance of the chemiluminescence in the reactions of Grignard reagents.[28,32–35] In the first place it was shown that the chemiluminescence in the oxidation of Grignard reagents by oxygen is a fairly general phenomenon for compounds of this class. Among the 60 Grignard reagents tested by Dufford et al.[24] 40 proved to be capable of chemiluminescence.

A list of these compounds, supplemented by the data of Evans and Diepenhorst[34] with indication of the colour and brightness of the chemiluminescence, is presented in Table 1; data for the chemiluminescence of these compounds in the reactions with chloropicrin and bromopicrin are included for comparison. The type of organic group plays a significant role in the appearance of chemiluminescence in the oxidation of Grignard reagents by oxygen. Compounds with isocyclic organic groups emit more light than those with acyclic groups. A favourable factor for both types of compounds is the presence of a direct bond between magnesium and an unsaturated carbon atom. Among isocyclic derivatives of Grignard reagents, the chemiluminescence is more intense in the reactions of compounds containing an aromatic group. The substitution of one hydrogen atom in the benzene ring by another atom or group leads to an increase of the brightness of the chemiluminescence. The position of the substituent in the benzene ring relative to magnesium is then a decisive factor:[34] The brightness of the chemiluminescence decreases in the sequence *p*- > *o*- > *n*. When the position of the substituent and the chemical nature of the group are the same, the chemiluminescence is more intense for bulkier groups. A change in the chemical nature of the substituent X in RMgX (where R is an aromatic group and X = halogen or CH_3) leads to a decrease of the brightness in the sequence chlorine > ethyl > bromine > iodine.[24,34]

Table 1. Characteristics of the reactions of Grignard reagents in ether accompanied by the brightest chemiluminescence.[24,34]

Compound	Brightness of chemiluminescence in reactions with:		
	O_2	chloropicrin	bromopicrin
p-ClC_6H_4MgBr	v.br.b	w.	nil
p-BrC_6H_4MgBr	v.br.b	v.br	nil
β-$C_{10}H_7MgBr$	v.br.b.	–	–
α-$C_{10}H_7MgBr$	br.g.-b.	nil	nil
p-$ClC_{10}H_6MgBr$	br.g.-b	–	–
C_6H_5MgCl	br.g.	w.	v.w.
C_6H_5MgBr	br.b.	w.	v.w.
o-BrC_6H_4MgBr	br.b	–	–
m-BrC_6H_4MgBr	br.b	–	–
p-ClC_6H_4MgI	br.b.	–	–
p-$ClH_3C_6H_4MgBr$	br.g.-b.	w.	–
p-$CH_3C_6H_4MgI$	br.b.	br.g.	nil
p-$C_2H_5C_6H_4MgBr$	br.b.	m.	m.
p-$C_4H_9C_6H_4MgBr$	br.b.	–	–
p-$C_6H_5C_6H_4MgBr$	br.b.	–	–
p-(*p*'-BrC_6H_4)C_6H_4MgBr	br.g.	–	–
p-, *o*-$(CH_3)_2C_6H_3MgBr$	br.y.-wh.	–	–

Notation: v.br. = very bright; m. = moderate; b. = blue; g. = green; y.-wh. = yellow-whitish [w = weak; v.w. = very weak].

An increase of the number of substituents (more than one) in the benzene ring entails a decrease of the brightness of the flow.[35] Chemiluminescence is observed also for Grignard reagents based on naphthalene and anthracene derivatives in which the MgBr group is in the β-position.

The chemical nature of the solvent (14 different ethers, benzene, and dimethylaniline were tested) does not have a significant influence on the intensity of the glow[34] and the observed differences in brightness are caused by the different solubilities of the Grignard reagents and by the viscosity of the medium. Thus the different stabilities of the etherates of the Grignard reagents do not exert the influence suggested in earlier studies.[31,36]

The nature of the substituent and its position in the benzene ring have an appreciable influence also on the spectroscopic characteristics of the chemiluminescence. It has been found[24] that, in each of the two series of Grignard reagents C_6H_5MgCl, C_6H_5MgBr, C_6H_5MgI and *p*-$CH_3C_6H_4MgCl$, *p*-$CH_3C_6H_4MgBr$, *p*-$CH_3C_6H_4MgI$, the compounds containing chlorine give rise to a longer-wavelength (green light) chemiluminescence, while those containing iodine produce the shortest-wavelength (blue light) chemiluminescence. A similar effect has been observed also for the dihalogeno-derivatives of Grignard reagents: *p*-ClC_6H_4MgCl, *p*-BrC_6H_4MgBr, and *p*-IC_6H_4MgI. When the position of the substituent in the benzene ring relative to magnesium is varied in each of the Grignard reagents investigated, namely $CH_3C_6H_4MgCl$, $CH_3C_6H_4MgBr$,

$CH_3C_6H_4MgI$, ClC_6H_4MgBr, BrC_6H_4MgBr, and ClC_6H_4MgCl, the wavelength of the emission increases in the sequence *m*- < *o*- < *p*- (from violet to green light).[24]

When a solution of the Grignard reagent being oxidised was acted upon by ultraviolet light, a photoluminescence (PL), whose intensity increased with the degree of oxidation, was observed; the initial Grignard reagent did not exhibit a photoluminescence.[30,34,37] Neither phosphorescence nor X-ray luminescence were observed for the products of the oxidation of the Grignard reagents. As a rule, the photoluminescence spectra differed from the chemiluminescence spectra.[30,34,37] The chemiluminescence spectra of Grignard reagents containing chlorine or bromine in the benzene ring (*p*-ClC_6H_4MgBr, *p*-BrC_6H_4MgBr) consisted of a single band extending from 448 to 518 nm.[30] The chemiluminescence and photoluminescence of the Grignard reagents derived from naphthalene each contained one band with markedly different maxima.[34] A bathochromic shift of the bands has been observed in the oxidation of these Grignard reagents and has been attributed to the unusual effect of the emitted chemiluminescence as light exciting the photoluminescence of the oxidation products in a longer-wavelength part of the spectrum. The above differences between the chemiluminescence and photoluminescence spectra led to the conclusion[38] that the nature of the chemiluminescence and photoluminescence emitters is different. The bright photoluminescence occurring in the oxidation of Grignard reagents has been attributed[37] to the emission by ROMgX (where R is an aromatic group and X is a halogen).

In later investigations[20,25,27] the identification of the emitters responsible for the glow, achieved with the aid of a sensitive spectroscopic technique, showed that the chemiluminescence and photoluminescence are caused by the emission of light from the same substances but of a kind different from ROMgX. The spectroscopic characteristics have been obtained in the oxidation by oxygen of solutions of C_6H_5MgBr and *p*-ClC_6H_4MgBr in THF, diethyl ether (Fig. 3),[27] and benzene with an admixture of triethylamine.[26] The nature of this solvent does not influence the form of the spectra. The difference of the chemiluminescence spectra from those obtained previously in studies[34,37] where the emission was detected mainly in the visible region and did not coincide with the photoluminescence spectra of the oxidation products has been attributed[20] to the internal filter effect caused by the high concentrations (1 M) of the solutions of Grignard reagents. It was found that it is essential to apply corrections for this effect at low concentrations of Grignard reagents (10^{-3} M). Although Bardsley and Hercules[20] and Bolton and Kerns[27] obtained identical chemiluminescence spectra, they identified different oxidation products as the emitters. Bolton and Kerns[27] found that excited molecules of brominated biphenyls arise in the oxidation of C_6H_5MgBr and *p*-ClC_6H_4MgBr. The photoluminescence spectra of these substances, obtained by the photolysis of bromobenzene (or 1-bromo-4-chlorobenzene) in ether or by the thermolysis of benzoyl peroxide in bromobenzene, were identical with the photoluminescence spectra of the solutions after the oxidation of C_6H_5MgBr or *p*-ClC_6H_4MgBr respectively and with the chemiluminescence spectra of these Grignard reagents. However, it was not discovered which compounds are responsible for the photoluminescence in the longer-wavelength part of the spectrum, which is excited selectively by the 366 nm line in the light from the mercury lamp (instead of the 313 nm which excites both components of the photoluminescence spectrum). Bardsley and Hercules[20] suggested that the emitter is *p*-terphenyl $C_6H_5C_6H_4C_6H_5$—another product of the oxidation of phenylmagnesium bromide. According to Bolton and Kerns,[27] this identification is erroneous because Bardsley and Hercules[20] compared the chemiluminescence spectrum with an incorrect photoluminescence spectrum of *p*-terphenyl. The actual position of the photoluminescence maximum in the spectrum of *p*-terphenyl (340 nm) according to data in Berlman's book[39] differs markedly from the chemiluminescence peak/365 nm). After the oxidation of *p*-ClC_6H_4MgBr, three fractions exhibiting a blue photoluminescence were isolated[20] by chromatographic separation. The only product identified in these fractions (it is suggested that it is $ClC_6H_5C_6H_4C_6H_5Cl$) has a photoluminescence spectrum (with a maximum at 345 nm) which does not coincide with the chemiluminescence spectrum. Two other products, which were unidentified because of their small amount, exhibit a photoluminescence at 377 and 387 nm, i.e. in the region of the chemiluminescence maxima. Estimations of the quantum efficiency of the chemiluminescence[20] yielded 10^{-6} and 10^{-4} for C_6H_5MgBr and *p*-ClC_6H_4MgBr respectively.

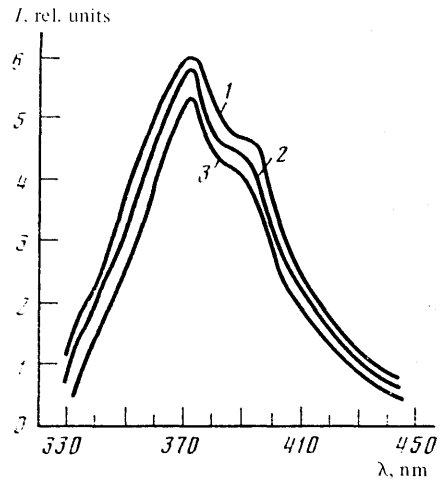


Figure 3. The fluorescence spectrum of the products of the oxidation of phenylmagnesium bromide in diethyl ether[27] with an excitation wavelength λ_e = 313 nm (curve *1*), the fluorescence spectrum of photolysed bromobenzene in ether with λ_e = 313 nm (curve *2*), and the chemiluminescence spectrum in the reaction of a solution of phenylmagnesium bromide in ether with oxygen (curve *3*).

The glow of brominated biphenyls is excited in the elementary reaction step and not as a result of energy transfer,[27] but the introduction of brightly fluorescent additives does not influence the chemiluminescence intensity. It was found that the oxidation of diphenylmagnesium is not accompanied by chemiluminescence.[27] In the same study it was also shown that the unsubstituted biphenyls formed in the oxidation of phenylmagnesium bromide (in yields up to 15%) are not excited in this chemiluminescence system. An EPR signal was detected in the oxidation of phenylmagnesium bromide,[27] which is important, since previously the formation of free radicals in the oxidation of organomagnesium compounds had been demonstrated on the basis of more indirect data: the analysis of the composition of the oxidation products and the study of the stereochemistry of the autoxidation reaction.[40]

Two mechanisms of the oxidation reaction, ensuring sufficient energy for the excitation of the chemiluminescence of brominated biphenyls (90 kcal mol^{-1}), have been proposed.[27] According to the first mechanism, the excitation takes place as a result of the reactions of free radicals:

$$C_6H_5MgX + O_2 \rightarrow C_6H_5O_2MgX \rightarrow C_6H_5^{\cdot} + MgO_2X \xrightarrow{MgX_2}$$
$$\rightarrow C_6H_5MgX + \dot{X} \rightarrow XC_6H_5MgX^{\cdot} \xrightarrow{R} R^{\cdot} + XC_6H_5MgX \xrightarrow{O_2} XC_6H_5O_2MgX \rightarrow$$
$$\xrightarrow{C_6H_5MgX} \begin{cases} \longrightarrow XC_6H_5MgX + C_6H_5OMgX; \\ \longrightarrow 2MgOX + XC_6H_5C_6H_5^{\cdot} \rightarrow XC_6H_5C_6H_5 + h\nu. \end{cases}$$

It follows from the above mechanism that the emitter is excited on interaction of the organomagnesium peroxide with the initial Grignard reagent. However, no direct evidence for the involvement of the peroxide in the generation of the chemiluminescence has been presented.[27] The low intensity of the EPR signal precluded the identification of the radicals. In order to demonstrate the involvement of the radicals in the chemiluminescence, an attempt was therefore made to investigate the influence of radical trapping agents on the chemiluminescence; the attempt was unsuccessful because of the low solubility of such agents and (or) their interaction with the Grignard reagent. The authors[27] proposed a second, alternative mechanism without the participation of free radicals:

$$C_6H_5MgX + O_2 \rightarrow C_6H_5O_2MgX \xrightarrow{C_6H_5MgX}$$
$$\rightarrow 2C_6H_5OMgX \rightarrow C_6H_5C_6H_5X^{\cdot} + MgO + MgOX;$$
$$\rightarrow C_6H_5C_6H_5X + h\nu.$$

We may note that these investigators[27] do not give preference to either of the two mechanisms.

2. The Influence of the Magnetic Field

The influence of the magnetic field on chemical reactions is regarded nowadays as a reliably established fact[41–43] although up to 1967 the existence of this effect appeared extremely doubtful.[41] The study,[44] which is apparently the first investigation in which the sensitivity of a chemical reaction to the magnetic field was observed (at any rate, this is absolutely certain in relation to reactions accompanied by chemiluminescence) is of special interest in this connection. The authors[44] thought that in a strong magnetic field there is a possibility of identical orientations of the molecules or molecular orbitals, which may result in the polarisation of the emitted light. They did not observe the polarisation of the chemiluminescence but were able to discover another effect, which consists in an increase of the intensity of the chemiluminescence when the Grignard reagent is oxidised in the magnetic field. The rapid imposition of the field induces a directional flow of a stream of solution and an increase of the brightness of the emission from the sides of the metallic crucible containing the solution. The authors[44] explained the observed phenomenon by the movement of the products of the oxidation of the Grignard reagent, which possess paramagnetic properties, towards the poles of the magnet. This effect has been clearly observed for *p*-BrC_6H_4MgBr only in strong fields (1500 G).

3. Electrochemiluminescence of Solutions of Grignard Reagents

A glow has usually been observed under severe electrolysis conditions (at potentials ranging from 100 to more than 1000 V),[44,45] with the exception of one study,[46] where, apart from the fact that electrochemiluminescence (ECL) has been detected, no other data concerning the glow of the Grignard reagent were presented. For solutions of C_6H_5MgBr or $C_6H_5CH_2MgBr$ in ether (potential 110–130 V, platinum plate electrode, current 0.02 A), the brightness of the observed ECL was so great that in the case of phenylmagnesium bromide the outline of the anode could be distinguished in a dark room at distances up to 6 m.[45]

A larger series of Grignard reagents has been investigated by Dufford et al.[44] A bright glow has been observed for Grignard reagents based on phenyl bromide (visible at 110 V), *p*-iodotoluene, and 1,4-bromochloronaphthalene (appears at a potential of 500 V); a weak glow has been found for n-lauryl bromide (visible only at a potential >1000 V) and a very weak glow has been observed for *m*-bromochlorobenzene (even at 1500 V the ECL is weaker than the chemiluminescence of this compound in its reaction with O_2) and for α-bromonaphthalene; there is no glow in the case of benzyl chloride. The glow is usually excited at the anode and more rarely at the cathode or at both electrodes. A number of compounds, for which chemiluminescence is not excited in their reaction with oxygen, emit light during electrolysis.

A glow during electrolysis has been observed reliably in all cases for compounds with a brighter chemiluminescence; however, the brightness of the emission in electrolysis and in oxidation by oxygen is a maximum for different Grignard reagents. On this basis, it has been concluded[44] that the nature of the glow is different in these processes. In contrast to this, in another study[45] it has been suggested that the mechanisms of the chemiluminescence and the ECL of solutions of Grignard reagents are identical and involve electron transer.

The electrolysis of Grignard reagents is accompanied by the precipitation of metallic magnesium, which exhibits a high catalytic activity.[44,45] One cannot rule out the possibility that this catalytic activity of magnesium influences also the chemiluminescence.

The modern interpretation of the mechanisms of electrode processes involving organomagnesium compounds includes reactions with participation of radicals (organic and organomagnesium radicals):[47]

$$R_2Mg \rightarrow R^{\cdot} + RMg^{\cdot}$$
$$RMg^{\cdot} \rightarrow Mg + R^{\cdot}$$

Consequently, there is a possibility of the excitation of the ECL of solutions of Grignard reagents in radical reactions. Admittedly these reactions reflect processes at the cathode (which is associated with the polarographic method of investigation), whereas, as stated above, the ECL is mainly observed near the anode. It is noteworthy that the glow excited at very high potentials (above 1000 V) is hardly a pure example of the classical ECL and its nature may be similar to that of the emission of light accompanying the so-called non-Faraday electrolysis.[5]

The ECL of phenylmagnesium bromide has been investigated at low potentials (starting with 10 V).[25] The electrolysis was carried out in carefully deoxygenated solutions. After a short time, the glow disappears spontaneously despite the continuous passage of current through the solution without an appreciable consumption of the Grignard reagent. Subsequently this was demonstrated successfully on the basis of the chemiluminescence which arises following the subsequent admission of air into the solution which ceased to emit light during electrolysis. One can therefore conclude that in this case the anodic emission of light is associated with the presence of impurities, containing O_2, the liberation of which takes place as a result of the slow decomposition of the impurities during electrolysis.

Thus, in order to determine the mechanism of the ECL of solutions of Grignard reagents and also to demonstrate the very fact that such a glow takes place, it is necessary to carry out additional experiments with a clear separation of the anodic and cathodic cell compartments and with determination of the compositions of the anolyte and catholyte.

4. Oxidation of Grignard Reagents by Organic Peroxides

The chemiluminescence accompanying the interaction of solutions of Grignard reagents with benzoyl, ethyl, and diacetone peroxides has been observed by Gilman and later confirmed by Dufford et al.[38] The reaction of BP with a number of Grignard reagents (C_6H_5MgBr, p-BrC_6H_4MgBr, p-ClC_6H_4MgBr) is accompanied by the emission of light with a lower intensity than in the oxidation of these Grignard reagents by oxygen.

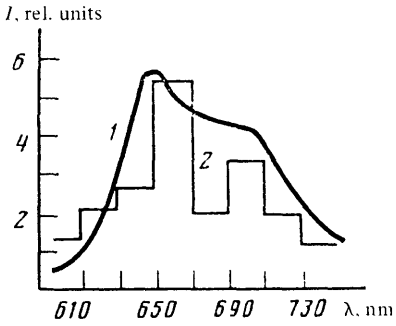


Figure 4. The fluorescence spectrum of a solution of the triphenylmethyl radical in diethyl ether (10^{-4} M) with λ_e = 447 nm (curve *1*) and the chemiluminescence spectrum in the reaction of phenylmagnesium bromide with benzoyl peroxide in ether (line 2).[48]

A detailed investigation of the mechanism of the chemiluminescence arising in the reaction of C_6H_5MgBr, ClC_6H_4MgBr, and $CH_3C_6H_4MgBr$ with BP and t-butyl peroxybenzoate in THF and diethyl ether[48] is of special interest. The reactions with diphenylmagnesium and with aliphatic Grignard reagents did not give rise to a glow. The oxidation of phenylmagnesium bromide is accompanied by a very bright (visible to the naked eye) red glow and the colour of the solution then changes from pale-brown to red. The excess peroxide produces a yellow colour owing to the formation of the triphenylmethyl radical, which was characterised by its EPR spectrum and by comparison with the spectrum of the radical synthesised independently. The radical is very stable: on storage in a sealed vessel the EPR signal remains unchanged for a month. The same radical has been identified as the chemiluminescence emitter. (Probably this is a unique case of the chemiluminescence of solutions where the radical is an emitter of the glow associated with a chemical reaction). The emitter has been identified on the basis of the identity of the chemiluminescence spectrum and the photoluminescence spectra of the products of the reaction of BP with phenylmagnesium bromide and a solution of the triphenylmethyl radical (Fig. 4). The time corresponding to a decrease of the chemiluminescence intensity by 50% depends on the nature of the solvent. The chemiluminescence emitter is excited in an elementary reaction step, since in the presence of fluorescent additives (pentacene, rubrene, and rhodamine G) the brightness of the chemiluminescence does not increase.

In order to determine the mechanism of the formation of the triphenylmethyl radical, a study has been made[48] of the reaction of deuteriated phenylmagnesium bromide with peroxide. The EPR signal of the resulting radical is three times wider than in the reaction of the protonated Grignard reagent, which the authors interpreted as evidence for the formation of the triphenylmethyl radical from one of the benzene rings of the Grignard reagent and two peroxide rings. The formation reaction of this radical is a side reaction in relation to the main interaction of the Grignard reagent with the peroxide. This is associated with the low yield of the radical compared with the yield of the stable oxidation products (the interaction of 0.1 M C_6H_5MgBr with an excess of the peroxide produces 10^{-4} M triphenylmethyl radical). However, when the reaction conditions are altered, it is possible[48] to increase the yield of the radical and hence also the chemiluminescence intensity.

5. The Interaction of Grignard Reagents with Other Substances

When a number of substances (H_2O, N_2O, H_2O_2, SO_2, CO, NO_2, H_2, N_2, NO, CO_2, and Na_2O_2) come into contact with solutions of Grignard reagents, a glow does not appear even when highly exothermic reactions take place (with Na_2O_2, H_2O_2, and H_2O).[28,31,32] The appearance of chemiluminescence in the reactions of certain Grignard reagents with benzene triozonide has been mentioned.[24] A bright-red chemiluminescence has been observed[25] in the reaction of phenylmagnesium bromide with carbon tetrachloride in diethyl ether. This extremely vigorous reaction results in the formation of the triphenylmethyl radical. However, in the absence of oxygen chemiluminescence is not observed; the autoxidation of the triphenylmethyl radical is also not accompanied by a glow.

6. The Oxidation of Organocalcium Compounds by Oxygen

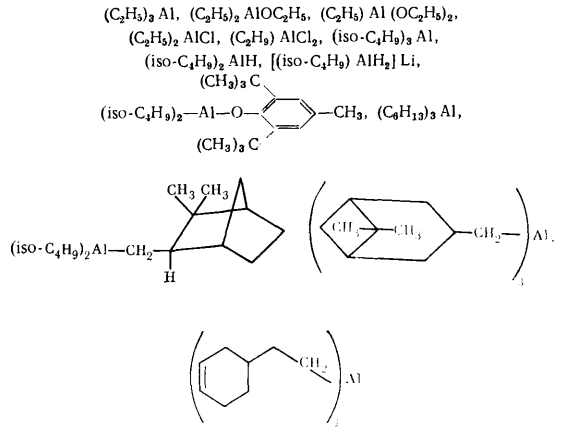
The organocalcium compound C_6H_5CaI was synthesised for the first time by Thomas and Dufford[35] and a yellow chemiluminescence was observed in its oxidation with oxygen. The not unduly high intensity of this chemiluminescence is comparable to that of the chemiluminescence in the analogous reaction of C_6H_5MgI. The alkyl derivative C_2H_5CaI does not chemiluminesce in its reaction with oxygen. A similar negative result has been obtained for organomercury[35] and organozinc[24] compounds: C_6H_5ZnBr, C_6H_5ZnI, and p-BrC_6H_4ZnBr.

IV. THE CHEMILUMINESCENCE OF SOLUTIONS OF ORGANOALUMINIUM COMPOUNDS AND THE ELECTROCHEMILUMINESCENCE OF A RHENIUM CARBONYL SOLUTION

1. Oxidation By Oxygen

The chemiluminescence in the oxidation of organoaluminium compounds (OAC) in solution by oxygen has been observed comparatively recently.[49] There is no information about the chemiluminescence of organic compounds of other Group III elements. The ability to enter into a reaction with oxygen

accompanied by chemiluminescence proved to be a characteristic property of solutions of OAC: a glow has been detected for trialkylalanes with different numbers of carbon atoms (C_2–C_6), their hydride and halogeno-derivatives, a complex of the hydride with an alkali metal, derivatives of norbornene, and other OAC:[49–51]



The kinetic plots of the chemiluminescence intensity obtained when air (or oxygen) is bubbled through solutions of the above OAC, have a feature in common: they exhibit one or several luminescence intensity maxima, which indicates the excitation of the chemiluminescence in reactions of intermediates in the oxidation of the OAC. The brightest chemiluminescence has been observed in the oxidation of the complex $[(iso\text{-}C_4H_9)_2AlH_2]Li$;[50] a bright glow has been noted in the oxidation of diisobutyl(2,6-di-t-butyl-4-methylphenoxy)-aluminium.[50]

The quenching of the chemiluminescence by oxygen and the luminescence yield for the primary emitter made it possible to postulate compounds containing the carboxy-group as the likely chemiluminescence emitters.[51] The increase of the brightness of the chemiluminescence following the replacement of the alkyl group in $(iso\text{-}C_4H_9)_3Al$ by the norbornane group is apparently associated with the high yield of ketones in the oxidation of the norbornane derivative. For certain OAC of this kind, the yield of ketones reaches 90%, while in the oxidation of alkyl derivatives ketones are side products.[13]

The brightness of the chemiluminescence in the oxidation of OAC by oxygen (in contrast to the oxidation of Grignard reagents) increases when a fluoroscent additive (9,10-dibromoanthracene) is introduced into the solution. It has been established that the increased chemiluminescence intensity is caused by the sensitising action of this additive, since the rate of oxidation and the form of the kinetic curve do not change under these conditions and the chemiluminescence spectrum coincides with the photoluminescence spectrum of 9,10-dibromoanthracene.[51] The intensification coefficients of the brightness of the chemiluminescence in the presence of identical amounts of the additive depend on the nature of the OAC and diminish in the sequence diisobutyl(isocamphenyl)aluminium (74) > trimyrtanylaluminium (27) > diisobutyl(2,6-di-t-butyl-4-methylphenoxy)aluminium (2).[50] Thus the primary chemiluminescence emitters in the oxidation of these OAC are of different kind and have different luminescence yields.

Three luminescence regions have been differentiated on the kinetic plot of the chemiluminescence intensity in the oxidation of triethylaluminium: two maxima and a long low-slope descent (Fig.5).[51] This kinetic relation indicates the occurrence of several reactions, accompanied by chemiluminescence, of the intermediates formed in consecutive stages. We may note that similar information can be found just as explicitly from the monotonic kinetic variation of the amount of absorbed oxygen, usually obtained in the study of the kinetics of the oxidation of OAC. The complexity of a more detailed interpretation of the kinetic chemiluminescence plot obtained can be understood when a simplified mechanism, reflecting the overall oxidation reaction of trialkylalanes, is considered taking into account the reactions undergone by organoaluminium peroxides:

$$AlR_3 \xrightarrow{O_2} \underset{(I)}{R_2Al(OOR)} \rightarrow R_2Al(OR) \xrightarrow{O_2} \underset{(II)}{RAl(OR)(OOR)};$$

$$RAl(OR)_2 \xrightarrow{O_2} \underset{(III)}{Al(OR)_2(OOR)} \rightarrow Al(OR)_3;$$

$$RAl(OR)(OOR) + AlR_3 \rightarrow RAl(OR)_2 + R_2Al(OR); \quad (1)$$

$$RAl(OR)(OOR) + R_2Al(OR) \rightarrow 2Al(OR)_2; \quad (2)$$

$$RAl(OR)(OOR) + RAl(OR)_2 \rightarrow 2Al(OR)_3; \quad (3)$$

$$R_2Al(OOR) \rightarrow RAl(OR)_2; \quad (4)$$

$$RAl(OR)(OOR) \rightarrow Al(OR)_3. \quad (5)$$

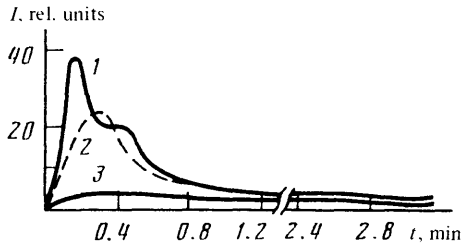


Figure 5. Time variation of the chemiluminescence intensity in the oxidation of solutions of OAC (2.9×10^{-2} M in toluene at 20 °C: *1*) triethylaluminium; *2*) the oxide; *3*) the dioxide.[51]

On the basis of data obtained by Razuvaev and co-workers[52] in a study of the dark oxidation of OAC, Tolstikov et al.[51] concluded that the chemiluminescence develops in a solution containing a complex mixture of OAC with different numbers of alkoxy-groups and organoaluminium peroxides [(I), (II), and (III)]. In order to discover the reactions accompanied by chemiluminescence, the stable oxidation products diethylaluminium ethoxide (oxide), ethylaluminium diethoxide (dioxide), and aluminium triethoxide (trioxide) were synthesised[51] by the reaction of triethylaluminium with ethanol.[51] It was shown that the interaction of these OAC in the absence of oxygen is not accompanied by chemiluminescence even in a highly exothermic reaction such as the formation of the oxide:

$$R_3Al + RAl(OR)_2 \rightarrow 2R_2Al(OR).$$

The interaction with oxygen of each of these OAC (except the trioxide) induces chemiluminescence, on the kinetic plot of which it is possible to differentiate one, two, and three luminescence regions (Fig.5) for the dioxide, oxide, and triethylaluminium respectively. The increase of the chemiluminescence intensity in this sequence is caused by the increased rate of oxidation of the OAC. The set of data

obtained, namely the dependence of the number of chemiluminescence intensity maxima on the number of alkoxy-groups in the OAC, the coincidence of the instant of the emission of the first chemiluminescence intensity peak with the dissociation of the first Al–C bond in triethylaluminium, and correlation of the effective activation energies for each of the three chemiluminescence maxima of triethylaluminium with the activation energies for the dark oxidation of triethylaluminium, the oxide, and the dioxide[52] enabled Tolstikov et al.[51] to conclude that the three regions on the kinetic plot of the luminescence intensity correspond to consecutive changes in the oxidation of the three Al–C bonds of triethylaluminium.

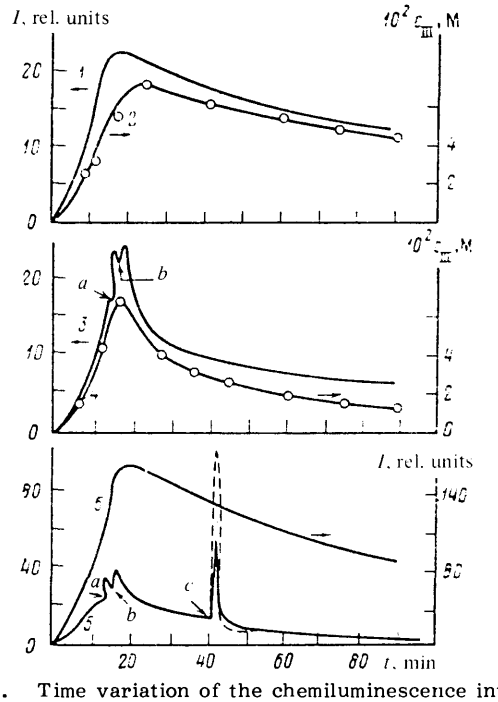


Figure 6. Time variation of the chemiluminescence intensity (curves *1*, *3*, *5*, and *6*) and of the concentration of the peroxide $Al(OR)_2(OOR)$ (III) (curves *2* and *4*) in the oxidation of a solution of the dioxide (0.3 M) in toluene at 20 °C:[51] *1*) and *2*) with constant bubbling of air; *3*) and *5*) the instants when the bubbling with air is stopped (*a*), the bubbling with argon is started (*b*), and the dioxide (continuous line) and the monoxide (dashed line) are added (*c*) are indicated; *6*) the chemiluminescence intensity after the addition of the activator (1×10^{-4} M).

The oxidation of the dioxide yielded parallel kinetic chemiluminescence intensity curves describing the analytical concentration of the organoaluminium peroxide (III) (the intermediate determined by the iodometric titration (Fig.6). The chemiluminescence intensity varies linearly with the concentration of the peroxide (III) (Fig.7). These results and also the absence of significant differences between the mechanisms of the oxidation of triethylaluminium and its alkoxy-derivatives permitted the conclusion that the appearance of chemiluminescence intensity maxima in the oxidation of all three OAC (triethylaluminium, the oxide, and the dioxide) reflects the accumulation and consumption of the corresponding peroxides (I), (II) and (III). We may note that the kinetic plot of the intensity of the chemiluminescence of triethylaluminium is the only experimental "monitor" which makes it possible to follow at the usual temperatures the formation and consumption of the highly reactive peroxides $(C_2H_5)_2AlOOC_2H_5$ and $(C_2H_5)Al(OOC_2H_5)(OC_2H_5)$, which had been previously [52,54] detected in solution only after extensive cooling of the latter.

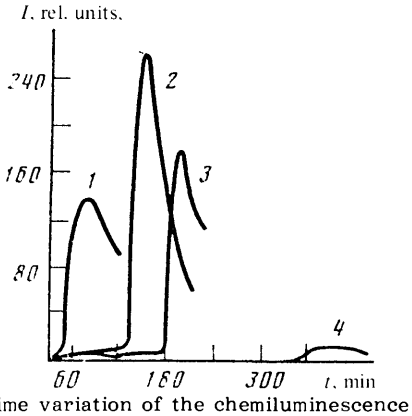


Figure 7. Time variation of the chemiluminescence intensity in the oxidation of solutions of $(C_2H_5O)_2AlC_2H_5$ in toluene in a closed volume (20 ml) under conditions of a constantly decreasing concentration of the dissolved O_2, in the presence of the 9,10-dibromoanthracene concentration [DBA] = 10^{-4} M at 20 °C, and at different initial concentrations of the dioxide (M): *1*) and *5*) 10^{-1}; *2*) 2.5×10^{-2}; *3*) 2.0×10^{-2}; *4*) 1.5×10^{-2}; curves *1–4* represent oxidation by oxygen.

The above reactions of organoaluminium peroxides are the main ones in the mechanism of the consecutive oxidation of the three Al–C bonds of trialkylalanes. In order to determine the contribution of each of these reactions to the excitation of the chemiluminescence, a more detailed study was made of the oxidation of the dioxide,[53] since this OAC has only one unoxidised Al–C bond.[55] Careful purification of this compound showed that only the activated chemiluminescence is observed in its oxidation, which is associated with the low contribution by the luminescence of the primary chemiluminescence emitter. The presence of a glow after the removal of oxygen from solution some time after the start of the oxidation of the dioxide established that the chemiluminescence is not excited in the peroxide formation stage, i.e.

$$(C_2H_5O)_2AlC_2H_5 + O_2 \rightarrow (C_2H_5O)_2AlOOC_2H_5, \qquad (6)$$

but arises in the interaction of the peroxide with the initial OAC:

$$(C_2H_5O)_2AlOOC_2H_5 + (C_2H_5O)_2AlC_2H_5 \rightarrow 2Al(OC_2H_5)_3. \qquad (7)$$

The removal of oxygen (Fig.6) leads merely to the acceleration of the decrease of the luminescence intensity, since the peroxide in consumed in the absence of the source from which it is generated [stage (6)].[51] The straight lines with the same slope $k = (1.9 \pm 0.1) \times 10^{-2}$ min^{-1} correspond to sections reflecting the decrease of the chemiluminescence

intensity and the concentration of the organoaluminium peroxide expressed in terms of semilogarithmic variables.[53] The ratios of the rate constants for the oxidation of the first, second, and third Al–C bonds in triethylaluminium are 100 : 25 : 0.96,[52,54,55] indicating the possibility of the simultaneous presence in solution of the dioxide, the oxide, and a small amount of triethylaluminium and the corresponding peroxides in the initial instant of the triethylaluminium oxidation reaction. Taking this into account as well as the chemiluminescence data for the oxidation of the dioxide and the intensification of the brightness of the chemiluminescence when the oxide and triethylaluminium are added to the solution after the removal of O_2 (Fig.6), one may conclude that the chemiluminescence in the oxidation of triethylaluminium is excited in the overall reactions (1), (2), and (3) and possibly also in the reaction

$$R_2AlOOR + R_3Al \rightarrow 2R_2Al(OR). \qquad (8)$$

The correctness of the identification of the above reactions of organoaluminium peroxides with OAC as the sources of the excitation of the chemiluminescence in the oxidation of the OAC by oxygen has been confirmed by the results of a study[56] in which chemiluminescence was observed in the interaction of triisobutylaluminium with the stable peroxide $(C_2H_5O)_2AlOOC(CH_3)_3$. The kinetic plot of the chemiluminescence intensity has a simpler form in this instance (without maxima), since the consumption of the organoaluminium peroxide is not complicated by the accumulation of the peroxide, as in the oxidation of the OAC by oxygen. It was found that oxygen plays a dual role in the chemiluminescence of OAC. On the one hand, it is essential for the excitation of the chemiluminescence as a source of peroxide and on the other it deactivates the glow.[51,53] The latter property of oxygen is manifested by the decrease of the chemiluminescence intensity when air is replaced by pure oxygen[51] and also by the presence of an induction period preceding the appearance of a brighter chemiluminescence in the oxidation of the dioxide under the conditions of the continuously decreasing concentration of dissolved O_2 (Fig.7).[53]

The addition of radical reaction inhibitors (diphenylamine or diphenylpicrylhydrazine) does not influence the chemiluminescence in the oxidation of OAC,[51] although it is known that these additives suppress the chemiluminescence in the oxidation of hydrocarbons.[3] The use of a more effective free radical trapping agent, namely the galvinoxy-radical (In),[53] induces the appearance of induction periods before the chemiluminescence is generated (when In is added before the start of the supply of O_2 to the solution) or a sharp decrease of the chemiluminescence intensity and the cessation of the absorption of O_2 (when In is added under the conditions of the excitation of the chemiluminescence) (Fig.8). On the grounds that the addition of In does not entail the complete disappearance of the chemiluminescence, the authors concluded[53] that the chemiluminescence in the oxidation of the dioxide by oxygen is excited in two types of reactions: free-radical and molecular reactions. We may note that the formation of free radicals in the interaction of organoaluminium peroxides with OAC has been unambiguously demonstrated only recently in a study[57] of the dark process.

2. Thermolysis of Organoaluminium Peroxides

Apart from the reaction with OAC, there exists another pathway for the consumption of the organoaluminium peroxide (OAP) in solution: thermal decomposition.[58–60] The possibility of the excitation of chemiluminescence in this process has been investigated[56] in relation to the thermolysis of a solution of the stable peroxide $(C_2H_5O)_2AlOOC(CH_3)_3$ in toluene free of O_2. This process is indeed accompanied by chemiluminescence, whose intensity increases with increase of temperature and the OAC concentration. At a constant temperature, the kinetic plot of the chemiluminescence intensity consists of two luminescence regions (Fig.9); in the first region the flash of chemiluminescence resulting from the addition of the OAC to the solvent is followed by a decrease of its intensity and in the second a sharp rise of the chemiluminescence intensity to a maximum followed by a prolonged descent is observed. The kinetic plot of the analytical concentration of the OAC has a simpler form (Fig.6, curve 2) i.e. yields less information.

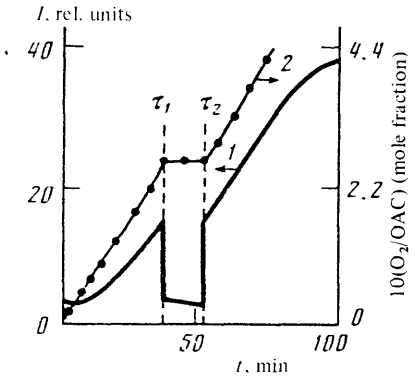


Figure 8. The influence of the addition of the inhibitor in the oxidation of a 10^{-1} M solution of $(C_2H_5O)_2AlC_2H_5$ in toluene on the chemiluminescence intensity (line *1*) and on the rate of absorption of O_2 (line *2*): [DBA] = 10^{-4} M; 20 °C; volume of solution 10 ml; [In] = 2×10^{-5} M; τ_1 = instant of addition of In; τ_2 = instant corresponding to the end of the induction period.

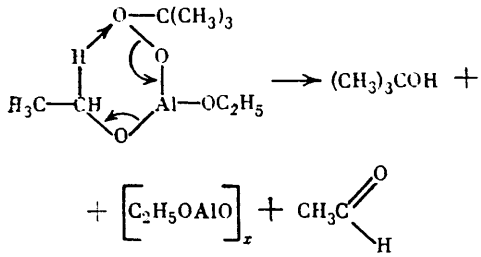
The existence of two thermolysis regions indicates the complexity of the thermolytic process, which has been interpreted in two ways in the literature concerned with the results of dark investigations: as heterolytic[57] or homolytic.[58] The second region in the kinetic plot of the chemiluminescence intensity (Fig.9), where a sharp rise has the form characteristic of the induced decomposition of organic peroxides, has been attributed[56] to the reactions of free radicals produced by the simultaneous dissociation of the O–O and Al–O bonds in the organoaluminium peroxide in conformity with the results of the study of the dark process:[58]

$$(C_2H_5O)_2AlOOC(CH_3)_3 \rightarrow (C_2H_5O)_2AlO^{\cdot} + (CH_3)_3CO^{\cdot};$$

$$(CH_3)_3CO^{\cdot} \rightarrow (CH_3)_2C{=}O + \dot{C}H_3.$$

The rate constant for the thermolysis of the OAP, calculated[56] from the slope of the linear form of the second section of the plot of the time variation of the chemiluminescence intensity (Fig.9*b*) agrees with the values $k = 7.4 \times 10^{-3}$ min^{-1} (T = 353 K) obtained[58] from dark measurements of the rate of decomposition of the same peroxide. The first luminescence region (Fig.9) has been assigned[56] to the consumption of the OAP as a result of the intramolecular oxidation of the ethyl fragment in the cyclic reactive complex, whose mechanism can be represented as follows in conformity with

the data obtained in the dark:[57]



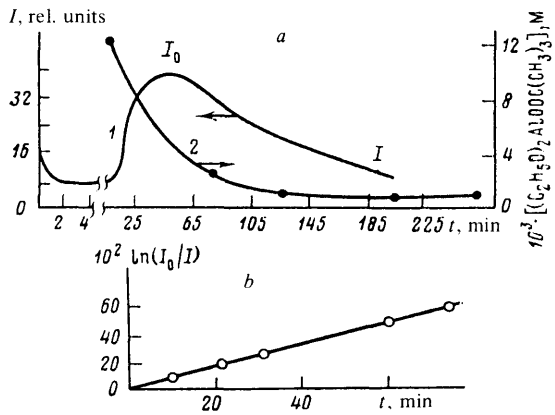


Figure 9. *a*) Time variation of the chemiluminescence intensity (curve *1*) and of the OAP concentration (curve *2*) in the thermal decomposition of the OAP (1.2×10^{-2} M) at 80 °C (the instant of the addition of the OAP to toluene heated to 80 °C was adopted as the starting point for the time readings); *b*) linear form of the I_0-I section in Fig. 9*a*.

The mechanisms presented above for the thermolysis and the homolytic and heterolytic decomposition of the OAP show that aldehydes and ketones, which frequently behave as emitters in the oxidation of hydrocarbons,[2] may be formed. The chemiluminescence spectra in the thermolysis of the OAP contain[56] three luminescence components with maxima at 430, 510, and 550 nm and, whereas the first two can be assigned to emission by excited ketones and aldehydes, the presence of the long-wavelength luminescence components indicates a more complex mechanism of the excitation of the chemiluminescence. In the presence of 9,10-dibromoanthracene the chemiluminescence spectrum corresponds to the emission by an excited activator.

The chemiluminescence data for the thermolysis of OAP show that, in the oxidation of OAC by oxygen, the chemiluminescence may be excited in reactions of two types: in the interaction with the OAC (a precursor of the OAP) or in the thermal decomposition of the OAP.

3. The Interaction of Organoaluminium Peroxides with Water

Yet another variety of the chemiluminescence of OAC has been observed recently, namely that associated with the interaction of OAP with water.[61] The addition of water to a solution of the dioxide being oxidised by oxygen intensifies appreciably the chemiluminescence. It has been shown that, among the series of highly exothermic reactions occurring in the oxidation of the dioxide by moist air in solution, only the reaction of water with the OAP—the intermediate in the oxidation of the dioxide—generates chemiluminescence.

This conclusion has been confirmed by the results of a study[56] where chemiluminescence was observed in the interaction of a stable OAP with H_2O in the absence of O_2 in the solution (Fig. 10). Two most probable mechanisms of the excitation of the chemiluminescence in the reaction of OAC with water have been proposed:[56] the recombination of the hydroperoxy-radicals with formation of an intermediate tetroxide by analogy with the chemiluminescence in the oxidation of hydrocarbons[9] and also the reaction of aluminium-containing radicals. The possibility of the formation of radicals in this system has been confirmed indirectly by the form of the kinetic plot of the chemiluminescence intensity (Fig. 10), which has a very pronounced threshold character.

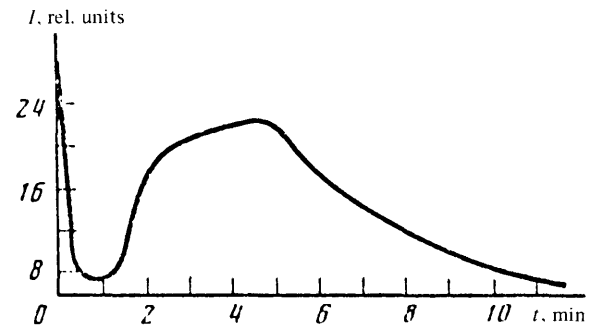


Figure 10. Time variation of the chemiluminescence intensity following the addition of H_2O to a solution of OAP in toluene after heating it for 220 min at 80 °C and then cooling (40 min) to 25 °C; $[OAP]_0 = 10^{-3}$ M; $[H_2O] = 1$ M.

The introduction of water into the system at the beginning of the oxidation of triethylaluminium or the oxide does not entail an increase in the brightness of the chemiluminescence compared with the "dry" oxidation of these OAC in view of the rapid consumption of the OAC owing to hydrolysis, as a consequence of which the OAP, namely $(C_2H_5)_2AlOOC_2H_5$ and $(C_2H_5O)_2AlOOC_2H_5$, do not accumulate in solution. There is no doubt that these highly reactive OAP should emit a brighter light in their reactions with water than in the reactions of $(C_2H_5O)_2AlOOC(CH_3)_3$ or $(C_2H_5O)_2AlOOC_2H_5$. This chemiluminescence can apparently be observed at low temperatures, where the above peroxides accumulate[52,54] in large amounts.

When water is introduced at later stages of the oxidation of triethylaluminium, a chemiluminescence flash is observed,[61] since the relatively stable peroxide $(C_2H_5O)_2AlOOC_2H_5$ has accumulated by that time as a result of the consecutive oxidation of the Al–C bonds in solution (Fig. 11). The brightness of the chemiluminescence in the reaction of this peroxide with water makes it possible to employ it for the quantitative selective determination of the OAP in solution. The generally adopted iodometric titration makes it possible to

determine up to 10^{-3} M peroxides, while 1.2×10^{-5} M peroxide in the presence of [DBA†] = 10^{-3} M can be determined from the linear dependence of the chemiluminescence intensity on the concentration of the OAP. An increase of [DBA] by an order of magnitude makes it possible to detect 10^{-6} M of the peroxide in solution.

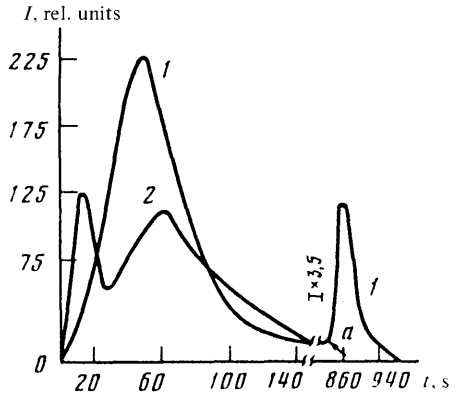


Figure 11. Time variation of the chemiluminescence intensity in the oxidation of a 1.8×10^{-2} M solution of triethylaluminium in toluene in the presence of an activator {[DBA] = 10^{-4} M}: *1*) oxidation with dry air (with addition of 10 ml of H_2O at time *a*); *2*) oxidation with moist air.

4. Oxidation of OAC Complexes with Oxygen

It has been found[62] that the addition of $Ru(bipy)_3Cl_2.6H_2O$ to the solution greatly increases the brightness of the chemiluminescence in the oxidation of OAC by oxygen. It has been established that the interaction of the ruthenium complex of the OAC with triisobutylaluminium, triethylaluminium, diisobutylaluminium hydride leads to the formation of the complex of the OAC with $Ru(bipy)_3Cl_2$ which is soluble in toluene and methylene chloride. The identity of the absorption and fluorescence spectra of the resulting complex demonstrated that ruthenium retains its oxidation state. The complex formation reaction is accompanied by the liberation of gaseous alkanes and the formation of alumino-oxanes—the products of the interaction of the water of crystallisation of the ruthenium compound with the OAC. Depending on the ratio of the amounts of the OAC and the initial ruthenium compound, the complex formed contains the initial OAC or the alumino-oxan as the ligand.

The oxidation of a homogeneous solution of the complex $[Ru(bipy)_3Cl_2(OAC)_n]$ with oxygen is accompanied by a bright-red chemiluminescence, which can be observed with the naked eye.[62] Comparison of the chemiluminescence and fluorescence spectra of the solution oxidised showed that the chemiluminescence emitter is the excited complex $[Ru(bipy)_3.Cl_2(OAC)_n]$. The difference between the forms of the kinetic chemiluminescence curves for the oxidation of the free OAC and their ruthenium complexes is not an adequate argument in support of the excitation of the chemiluminescence emitter in the elementary oxidation step or of an excitation via simple sensitisation, because of the difficulty of determining the exact composition of the ligand in the complex.

5. Electrochemiluminescence of a Rhenium Carbonyl Solution

Analysis of the data on the excitation of chemiluminescence in the redox reactions of OMC in solution permits the conclusion that the luminescence emitters are not the OMC themselves but either organic products of their reactions or the sensitisers introduced as additional species into the reaction zone. Admittedly one cannot rule out the possibility that light is emitted by excited species of the type RC–Al=O or similar formations produced when OAC are oxidised. The chemiluminescence, observed by Luong et al.,[63] in which the rhenium OMC has been reliably identified as the luminescence emitter, is therefore of special interest. The species involved in the chemical reaction and leading to the excitation of the rhenium carbonyl *fac*-$ClRe(CO)_3L$ (where L = 1,10-phenanthroline or 4,7-diphenyl-1,10-phenanthroline) were generated electrochemically. The process was carried out at platinum electrodes via cyclic electrolysis with the potential varied in the range from +1.3 to −1.3 V (in acetonitrile as the solvent). The luminescence emitter was excited by the annihilation interaction of the radical-anion and radical-cation produced by the electrochemical reduction and oxidation of the initial rhenium compound:

$$[fac\text{-}ClRe(CO)_3L]^{+\cdot} + [fac\text{-}ClRe(CO)_3L]^{-\cdot} \rightarrow 2\ [fac\text{-}ClRe(CO)_3L]^{\cdot}.$$

Comparison of the electrochemiluminescence and fluorescence spectra of the test solution showed that the luminescence emitter is the excited OMC.

V. THE CHEMILUMINESCENCE OF ORGANOMETALLIC COMPOUNDS IN THE GAS PHASE

The reactions of OAC with excited singlet molecular oxygen and with O and N atoms in the gas phase are accompanied by luminescence. Surprisingly, the gas-phase chemiluminescence of OAC has been first observed and investigated[64–66] not under laboratory conditions but in space in the vicinity of the Earth. This luminescence has been used to investigate the geophysical characteristics of the atmosphere (wind, turbulence, and molecular diffusion). For this purpose, liquid trimethylaluminium (1.1 kg)[64] or its mixture with triethylaluminium (20%)[65] was placed in a vessel containing nitrogen under a pressure of 25 atm. The OAC was evaporated in the twilight from a rocket despatched to a height of 85–160 km at a flight velocity of 1 km s^{-1}. This resulted in the formation of a chemiluminescent bluish-green cloud. The atomisation of liquid OAC proved more convenient for geophysical research than a hot mixture containing caesium nitrate and powdered metallic aluminium and magnesium.[64,65]

The luminescence quantum yield varied from 0.3 to 0.6 photons per trimethylaluminium molecule. The form of the glowing cloud resembled a cylinder 20 km long and 1.5 km in diameter. The cloud emitted an overall amount of energy of $10^{10.8}$ erg s^{-1}, which is equivalent to 2 kW; the power of the emission decreased with time in accordance with a kinetic curve having a single diffusion maximum.[64]

Simultaneously with the recording of the chemiluminescence, measurements were made of the kinetic and spectroscopic parameters of the fluorescence of the cloud excited by solar rays directed horizontally. The spectral intensity of this

†9,10-Dibromoanthracene (Translator).

fluorescence makes it possible to determine the temperature of the upper layers of the atmosphere. It was established[65] that the emitter of this chemiluminescence is AlO_2^*, emission being recorded in the form of a diffuse curve (Fig.12). The emitter is excited in the reaction of the intermediate AlO with the oxygen atoms present in the upper layers of the atmosphere: $AlO + O \rightarrow AlO_2^* \rightarrow AlO_2 + h\nu$. The presence of the intermediate (AlO) in this system has been confirmed by recording its blue-green fluorescence (Fig.12) excited by sunlight. The authors[65] put forward two possible pathways leading to the formation of AlO—via the reaction of trimethylaluminium with atomic or molecular oxygen.

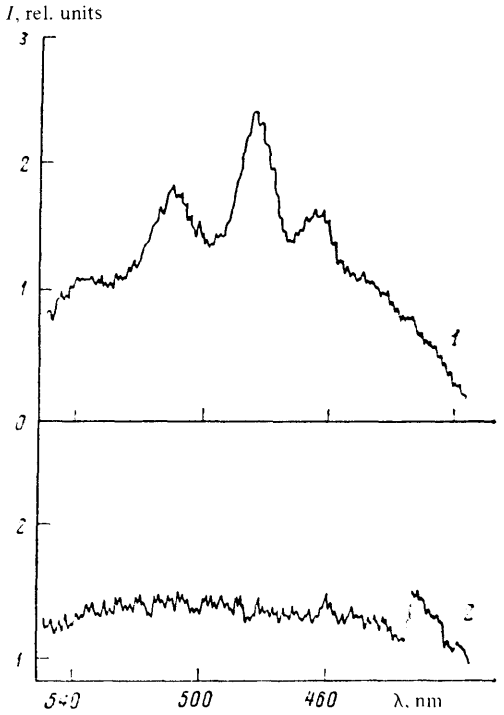


Figure 12. Emission spectra of triethylaluminium observed when the latter is sprayed from a rocket in space in the vicinity of the Earth; *1*) fluorescence spectrum excited by sunlight at a height of 138 km; *2*) chemiluminescence spectrum at a height of 92 km.

The relative contributions of the reactions of oxygen in various states to the gas-phase chemiluminescence were elucidated in laboratory investigations.[67] In these experiments pairs of OAC were introduced into an optically transparent chamber through which molecular oxygen, mixed with a carrier gas (argon) and subjected to a preliminary activation by a microwave discharge, was passed; this gas stream contains $O_2(a^1\Delta)$, $O_2(b^1\Sigma)$, and O atoms. The mixture composition was varied by removing O atoms as a result of the reaction with an HgO mirror deposited in the vicinity of the discharge unit or by introducing water vapour which selectively removes $O_2(b^1\Sigma)$. It was shown[67] that the presence of O atoms is not obligatory for the excitation of the chemiluminescence of trimethylaluminium, i.e. that the chemiluminescence in the upper layers of the atmosphere may be induced both by excited singlet oxygen $O_2(a^1\Delta)$ and O atoms. Without the preliminary activation of oxygen, a glow was not detected. Thus the chemiluminescence of OAC in the gas phase, in contrast to the liquid phase, is not excited in the reaction with molecular oxygen in the ground state.

Subsequent investigations[68,69] dealt solely with the reaction of trimethylaluminium with oxygen atoms. The absence of chemiluminescence in the reaction of trimethylaluminium with non-activated oxygen molecules was confirmed.[68] The authors[68] concluded that the recombination process of the type $AlO + O \rightarrow AlO_2^*$, proposed in earlier studies[64-66] as the excitation stage, is too slow compared with the rate of emission of light from the chemiluminescence cloud to be the source of the generation of the chemiluminescence. They suggested that the chemiluminescence emitter is AlO^* and not AlO_2^*.

A study[69] undertaken to eliminate these contradictions confirmed that the emission rate constant is indeed too high for reactions of the recombination type. However, here too AlO_2^* was identified as the chemiluminescence emitter; this was subsequently demonstrated with the aid of a high-resolution spectroscopic technique (to within 0.05 nm). In order to account for the discrepancies between the rates of emission and generation of chemiluminescence, the authors[69] postulated the existence of a second intermediate, which gives rise to AlO_2^* on reaction with O atoms:

$$RAlO + O \rightarrow AlO_2^* + R;$$

$$AlOR + O \rightarrow AlO_2^* + R.$$

The first process is believed to be energetically more favourable. In the reaction of trimethylaluminium, H_3CAlO has been suggested as an intermediate of this kind. The rate constant for the formation of the emitter via the suggested mechanism is 10^{-13} cm^3 s^{-1}.

A pink-white chemiluminescence has been observed[69] in the reaction of trimethylaluminium with N atoms obtained by activating nitrogen. The chemiluminescence spectrum consisted of well resolved bands, among which components in the red and violet parts of the spectrum predominated. The emissions due to CH and C_2 were grouped at 431.4 and 516.5 nm. Emission from Al at 507.8 and 572.6 nm was also identified. The transitions of Al(I) are manifested at 309, 394.4, and 396.1 nm.

The mechanism of the chemiluminescence, according to which all the methyl groups in the trimethylaluminium molecule are split off from the aluminium atom, was established on the basis of the spectroscopic data indicated; this results in the excitation of the residual aluminium atom. The most probable source of the excitation energy is the recombination of nitrogen atoms ($2N \rightarrow N_2$), in which 9.76 eV is evolved. The dissociation of three Al–C bonds requires an amount of energy of ~9 eV; the excitation energy of the aluminium atom is 4 eV. The following mechanism was proposed for the generation of the chemiluminescence:

$$(CH_3)_3Al + N \rightarrow AlN + 3CH_3;$$

$$AlN + N \rightarrow Al^* + N_2;$$

$$(CH_3)_3Al + 2N \rightarrow Al^* + N_2 + 3CH_3.$$

The existence of the intermediate AlN was demonstrated by means of the emission at 507.8 and 527.6 nm.[69]

Chemiluminescence has also been observed in the reactions of borine carbonyl with O and N atoms. There has been only one investigation of the chemiluminescence of organoboron compounds.[70] A technique analogous to that employed in the investigation of the chemiluminescence of OAC, supplemented by a mass-spectrometric unit for the determination of the composition and the amount of stable reaction products or

intermediates, was employed. The introduction of the complex H_3BCO into a stream of O atoms (in the absence of O_2) induced a dark-blue chemiluminescence in the range 270–390 nm. The chemiluminescence emitter was found to be BO^* (the $A^2\Pi \rightarrow X^2\Sigma$ transition) and the maximum emission was from the $v' = 4$ and $v' = 5$ levels, but emission from the $v' = 11$ and higher levels was also observed. In addition, a very weak glow of the O–H species ($A \rightarrow X$) was also manifested at 306.4 and 307.7 nm. In the presence of O_2, where the O atoms were generated by an electric discharge in an $He-O_2$ mixture, the chemiluminescence had a bright-pink colour. Its diffuse spectrum was mainly caused by the emission from BO_2^*, although here too there was also emission from BO^*.

In order to account for the observed mass spectra, the chemiluminescence, and the reaction stoichiometry, the authors[70] suggested that H_3BCO is decomposed via two possible initiation mechanisms. In the first of these O atoms remove the hydrogen atoms from the H_3B groups; the remaining fragments rapidly react with O atoms, giving rise to the highly excited BO, whose emission is in fact responsible for the chemiluminescence in the visible and near ultraviolet regions:

$$O + H_3BCO \begin{cases} \rightarrow OH + [CH_2BCO]^* \rightarrow OH + BH_2 + CO; \\ \rightarrow H_2O + [HBCO]^* \rightarrow H_2O + BH + CO. \end{cases}$$

The second possible pathway in the initiating stage involves the direct attack by the O atoms on the boron atoms with liberation of CO groups:

$$O + H_3BCO \rightarrow [H_3BO]^* + CO \begin{cases} \rightarrow BO + H_2 + H + CO; \\ \rightarrow HBO + H_2 + CO; \\ \rightarrow HBOH + H + CO; \\ \rightarrow H_2BOH + CO. \end{cases}$$

BO_2 is formed via the reaction

$$BO + O + M \rightarrow BO_2 + M;$$
$$BO + O_2 \rightarrow BO_2 + O.$$

The observed chemiluminescence is due to the last two reactions.

The interaction of H_3BCO with N atoms induces a bluish-green chemiluminescence, which could not be attributed to oxygen admixtures. The authors[70] believe that this chemiluminescence is not caused by the excitation of BN, whose radiative transitions ($^3\Pi \rightarrow X^3\Pi$) at 340–400 nm were recorded after the introduction of BCl_3 into a stream of activated nitrogen. The mechanism of this reaction is more complex than that in the H_3BCO-O system. The possibility of catalysis by one of the intermediates in the recombination reaction of nitrogen atoms has also been suggested.

The chemiluminescence in the reactions of Ni, Fe, Cr, W, Mn, and Co carbonyls with O, H, N, and inert gas (Ar, He, and Ne) atoms in metastable states has been investigated. One of the interesting aspects of the use of metal carbonyls is the gas-phase low-temperature (20–150 °C) generation of metal atoms from them in chemical reactions[71–74] on exposure to electric discharges[75–77] and on photolysis.[78–80] In all these processes some of the metal atoms are formed in an excited state, which leads to the appearance of a visually observable glow. The generation of a laser beam on the basis of Fe and Ni atoms in the ultraviolet and infrared regions of the spectrum has been achieved when the carbonyls of these metals were acted upon by discharges with a double electric pulse[75] and in the flash photolysis of $Fe(CO)_5$.[80] Only studies in which the excited states arose solely as a result of chemical reactions are examined below.

Chemiluminescence has been observed in the interaction of a number of metal carbonyls, namely $Cr(CO)_6$, $Mo(CO)_6$, $W(CO)_6$, $Fe(CO)_5$, $Ni(CO)_4$, $Mn_2(CO)_{10}$, and $Co(NO)(CO)_3$, with N atoms[71,72] and (for the first six carbonyls) also with O atoms.[72] A glow was also observed in the reactions of nickel and iron carbonyls with the inert gas (Ar, He, and Ne) atoms in metastable states. All these reactions were carried out at a reduced pressure (several mmHg) and were accompanied by emission from the excited states of the neutral metal atoms M. Metallic films were then deposited on the walls of the reactors.

The bright-blue chemiluminescence emission spectra in the interaction of metal carbonyls with nitrogen atoms consist exclusively of lines due to emission from neutral atoms.[71] In addition, an intense group of atoms has been noted[72] at 520 nm for the $Mo(CO)_6 + H$ and $Mo(CO)_6 + N$ reactions; they have been assigned to emission from Mo_2^*. On the basis of kinetic and spectroscopic reaction data, the continuous spectrum has been attributed to emission from MCO^*. The mechanism of the excitation of chemiluminescence in the reaction with N atoms includes a series of consecutive stages involving the decomposition of the carbonyls, i.e.

$$M(CO)_n + N \rightarrow M(CO)_{n-1} + NCO.$$

up to the formation of a free metal atom. The metal atoms are excited by collisions with nitrogen molecules in metastable states:

$$M + N_2^*(A^3N) \rightarrow M^* + N_2.$$

The latter are produced in a three-atom recombination reaction and have a short lifetime owing to their destruction on the walls of the reactor.

An analogous mechanism of the stepwise decomposition of the carbonyl has been proposed by Becker and Schurgers,[72] but they explain the excitation of the metal atoms by the retention of the energy, which the metals possess in the carbonyl complex, after the elimination of the CO groups. The chemiluminescence arising in the $M(CO)_n + O$ reaction, was assigned in their study to the emission from MO^*. This glow is observed for all the metals (Cr, W, Fe) investigated except for the molybdenum compound. It is suggested that the MO^* emitter is formed as a result of the direct interaction of oxygen atoms with the metal atoms formed when the CO ligands are removed from the carbonyl. Comparison of the rate constants for the overall reaction $M(CO)_n + O \rightarrow$ products with the rate constants for the reaction leading to chemiluminescence showed that a proportion (several %) of the steps in the overall reaction lead to the formation of substances in an excited state. No differences between the $M(CO)_n + H$ reaction and the $M(CO)_n + N$ (or O) reaction has been reported.[72]

The reactions of iron and nickel carbonyls with the metastable $Ar^*(^3P_2)$, $Ne(^3P_2)$, and $He(2^3S)$ atoms, obtained in a microwave discharge in a hollow cathode, are accompanied by a blue [for $Fe(CO)_5$] or reddish-blue [for $Ni(CO)_4$] chemiluminescence, readily observed with the naked eye.[73,74] The characteristic distinct spectral lines were assigned to the emission by the neutral metal atoms. The N_2 and OH^- emission bands are due to the luminescence by background impurities. The weak bands between 450 and 500 nm in the $Ne^* + Ni(CO)_4$ reaction spectrum are due to the (0,0) and (0,1) transitions of the excited CO^+ formed as a result of ionisation:

$$Ne^*(^3P_2) + CO(x, v=0) \rightarrow Ne + CO^+(A^2\Pi_i; v=0) + e^-.$$

The chemiluminescence intensity in the reactions of both carbonyls is described by linear relations as a function of the concentration of the metastable atoms X and the pressure

of the carbonyl (in the region of low pressures). Kinetic measurements showed that excited states of the metal are produced in the bimolecular process

$$X^* + M(CO)_n \rightarrow X + M^* + nCO.$$

The authors[73,74] found differences between the emission spectra of the metal atoms excited chemically and in an arc discharge.

Table 2. The chemiluminescence and electrochemiluminescence of OMC

Element	Compound	Second reagent	Medium
Li	C_6H_5Li	O_2	S, L
Li	C_4H_9Li	Benzoyl, lauryl, and t-butyl peroxides	L
Na	C_6H_5Na	O_2	S
K	C_6H_5K	O_2	S
Mg	RMgX, XRMgX	O_2	L
Mg	RMgX	Benzoyl, ethyl, and diacetyl peroxides, benzene triozonide, chloroform, carbon tetrachloride, aliphatic nitrocompounds, and picryl chloride	L
Mg	RMgX	Electrolysis	L
Ca	C_6H_5CaI	O_2	L
Al	R'_3Al, R'_2AlCl, $R'AlCl_2$, R'_2AlH, $[R'AlH_2]Li$, $[(R_3Al)_nRu(bipy)_3Cl_2]$, $[(>Al-O-Al<)_nRu(bipy)_3Cl_2]$	O_2	L
Al	R'_3Al, $(R'O)_2AlR'$	$(R'O)_2AlOOR$	L
Al	$(R'O)_2AlOOR'$	H_2O, thermolysis	L
Al	$(CH_3)_3Al$, $(C_2H_5)Al$	$O_2(a^1\Delta)$, O, N, He, Ar, Ne	G
B	H_3BCO	O, N	G
Mo	$Mo(CO)_6$	O, N, H, Ar, He, Ne	G
Cr	$Cr(RO)_6$	O, N, H, Ar, He, Ne	G
W	$W(CO)_6$	O, N, H, Ar, He, Ne	G
Mn	$Mn_2(CO)_{10}$	O, N, H, Ar, He, Ne	G
Fe	$Fe(CO)_5$	O, N, H, Ar, He, Ne	G
Co	$Co(NO)(CO)_3$	O, N, H, Ar, He, Ne	G
Ni	$Ni(CO)_4$	O, N, H, Ar, He, Ne	G
Re	*fac*-$ClRe(CO)_3L$	Electrolysis	L

Notation: S = solid phase, L = solution, G = gas; R = alkyl or aryl; R' = C_2–C_6 alkyls; in the reaction with O_2, R' represents in addition isocamphenyl, myrtanyl, or 3-(3-cyclohexenyl) ethyl [2-(3-cyclohexenyl)ethyl? Editor]; L = 1,10-phenanthroline or 4,7-diphenyl-1,10-phenanthroline.

VI. CONCLUSION

The summarising Table 2 shows that organic compounds of fifteen Group I–III and VI–VIII elements in the Periodic System are capable of chemiluminescence. However, we believe that chemiluminescence is a more general property of OMC, since the compounds of the majority of elements have not yet been tested in this respect and the available negative results in the literature refer to attempts to detect chemiluminescence with the naked eye. We believe that Table 2 reflects only a small proportion of the possible new chemiluminescence reactions of OMC.#

We shall now turn to the energy relations of the reactions. We may conclude that all the known light emitting reactions of OMC are highly exothermic, but by no means all highly exothermic reactions of OMC are accompanied by chemiluminescence. In the reactions with oxygen processes involving organometallic peroxides apparently play an important role in exciting the glow. However, this conclusion requires additional experimental confirmation. Thus the chemiluminescence in the reactions of compounds of Group I elements with oxygen has not been investigated at all. Whereas the involvement of intermediate peroxides in the excitation of the chemiluminescence of OAC in solution has been demonstrated fairly reliably, for Grignard reagents this is so far merely a hypothesis unsupported by experimental data.

The possibilities of the chemiluminescence method in determining the mechanism of the complex process involving the autoxidation of OMC has been demonstrated in a study of the influence of inhibitors on the chemiluminescence kinetics in the oxidation of OAC in solution. As regards the question of the involvement of free radicals in the excitation of the chemiluminescence of Grignard reagents, the available set of results obtained by the direct determination of these species by EPR in the oxidation of phenylmagnesium bromide by oxygen and in the study of the influence of magnetic fields on such luminescence can be interpreted as evidence for a free-radical mechanism. However, it is necessary to study in addition the influence on this chemiluminescence of trapping agents for free galvinoxy-radicals. It has been noted[40] that induction periods then appear in the oxidation of Grignard reagents.

The reactions of these OMC with oxidants other than organic peroxides, accompanied by a bright chemiluminescence, have so far remained almost uninvestigated. Among new types of reactions of OMC accompanied by chemiluminescence, we may note the glow in the thermolysis and hydrolysis of organoaluminium peroxides in solutions, the annihilation electrochemiluminescence of solutions of rhenium carbonyls, and the gas-phase chemiluminescence excited in the reactions of metal carbonyls with nitrogen, hydrogen, oxygen, and inert gas atoms in metastable states. It is of interest to note the difference between the mechanisms of the chemiluminescence in the oxidation of trialkylalanes by oxygen in the gas phase and in solution. In solution the chemiluminescence is excited as a consequence of the reaction of the OAC with molecular oxygen in the ground triplet state. In the gas phase the chemiluminescence is due to the reactions of the excited singlet oxygen.

The chemiluminescence of OMC has found practical applications. The use of the gas-phase chemiluminescence of organoaluminium compounds in the investigation of the geophysical characteristics of the cosmic space in the vicinity of the Earth is of interest. The chemiluminescence in the oxidation of OAC by oxygen in solution and the glow arising when water is introduced into the system attracts interest

#This is confirmed by a study which was published during the preparation of the review for the press: R.G.Bulgakov, G.Ya.Maistrenko, V.N.Yakovlev, S.P.Kuleshov, G.A.Tolstikov, and V.P.Kazakov, Dokl.Akad.Nauk SSSR (in the press). In this investigation chemiluminescence was observed for organic compounds of metals representing all the Groups in Mendeleev's Periodic System.

because of the possibility of their use to monitor the industrial synthesis of liquid alcohols at the stage involving the preparation of alkoxides by the oxidation of trialkylalanes. Measurement of the kinetics of the variation of the chemiluminescence intensity makes it possible to follow all the main reactions in the oxidation of triethylaluminium. The introduction of water into the system incorporating the OAC undergoing oxidation makes it possible to detect reliably the onset and end of the reaction involving the oxidation of the third Al–C bond in the trialkylalane.

Summarising the data presented, it is possible to differentiate several main aspects of the further development of the research into the chemiluminescence of OMC. Firstly, we have the study of the mechanism of the non-trivial pathway involving redox reactions of the OMC with formation of excited states. This will entail the solution of the problem of the mechanism of the overall photochemical processes, the identification of the chemiluminescence emitter, the elementary step in the excitation of chemiluminescence, the chemiluminescence yield, the influence of quenching agents, etc. Secondly, it will be necessary to investigate the possibility of using chemiluminescence in the study of the mechanism of the dark process, the determination of its nature (radical or molecular), the determination of the kinetic characteristics, and the determination of the influence of inhibiting or catalytic additives on the process mechanism and kinetics. In addition, the application of chemiluminescence in the analysis of both the OMC themselves as well as other substances interacting with the OMC or present in the reaction zone may prove to be promising. Finally, a comprehensive investigation of the possibility of devising methods for the chemiluminescence monitoring of industrial processes involving OMC is essential.

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Organic Reagents in Spectrophotometric Analysis

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The spectrophotometric analytical methods using organic reagents in modern chemistry are discussed. Certain new organic reagents, synthesised in recent years, are presented. New methodological procedures in spectrophotometric analysis and the possibilities of the available apparatus are examined. The advances achieved in the development of the theoretical principles of the action of organic reagents are described and a new approach to the explanation of the reactivity of organic compounds is put forward.
The bibliography includes 200 references.

CONTENTS

I. Introduction 1074
II. Principal characteristics of colour reactions 1074
III. New methods for increasing the efficiency of spectrophotometric analysis 1077
IV. The choice of organic reagents for the determination of individual elements 1079
V. Development of the theoretical principles of the action of organic reagents 1080

I. INTRODUCTION

The spectrophotometric methods are virtually the commonest methods in chemical analysis. Colour reactions of practical value have now been found for almost all inorganic ions. An increasing number of organic analytical methods are based on the corresponding colour reactions. The principal advantages of spectrophotometric methods is high sensitivity, universality (i.e. the possibility of determining both small and large amounts of substances), simple apparatus, and the possibility of automating the analytical procedure.

Spectrophotometric analysis is based on organic reagents (OR), whose number has been continuously increasing. At the same time the efficiency of their analytical action has increased: OR forming complexes with unusually high extinction coefficients of the order of several hundreds of thousands have appeared, which makes it possible to determine reliably 0.01 mg ml^{-1} of an element or even smaller amounts. The wide-scale automation of the methods requires the development of direct and rapid analytical procedures. This depends mainly on two factors: the selectivity and reliability of the reactions. By reliability, one understands the independence of the results of slight changes in reaction conditions and also only a slight influence of other substances present in solution on the main reaction. The most reliable results may be expected when OR interacting with the elements in acid media and not requiring the application of buffer solutions are used. The procedure employed in preparing the solution for the photometric measurements then reduces to simple dilution of the analytical solution with an acid (which, for example, makes it possible to carry out the analysis in a stream of liquid); furthermore, the possible interference associated with the hydrolysis of the ions and the formation of polymeric structures is reduced, which is especially important in the determination of certain rare and other, mainly heavy, readily hydrolysable elements such as Ti, Zr, Hf, Nb, Ta, and Pa. A series of effective OR which can be used in highly acid media have been proposed in recent years: arsenazo III and its analogues; antipyrine and its numerous derivatives; reagents of the triphenylmethane series; fluorones; azo-compounds based on pyrogallol, pyridine, and heterocyclic reagents, as well as many other groups and classes of OR.

A series of monographs[1-30] have been devoted to the theory and practice of the application of OR in photometry. These studies dealt with questions of the synthesis of the OR, their purification, and analysis,[8,12,20,27,28] the classification of the OR and the creation of an assortment of the latter suitable for individual elements,[2,7,9,12,15,20,23-25,29,30] the use of OR in spectrophotometric and luminescence measurements,[3,5,6,9,10,15,16,20,22,25] their use for the determination of organic substances[1] and anions,[21] and their application in ultra-microanalysis[4] and in extraction,[14,18] and also questions concerning the theory of the action of the OR.[2,7,8,9,20,23,24,26]

In the present review we shall confine ourselves to the consideration of the OR employed only in spectrophotometric and luminescence measurements. Attention is concentrated on azo-derivatives of chromotropic acid, because results important for the development of the theory of the action of OR have in fact been obtained in recent years precisely for these practically important OR. These results can be in many cases extended to other classes of OR.

II. PRINCIPAL CHARACTERISTICS OF THE COLOUR REACTIONS

The OR are organic compounds (monomeric or polymeric) of different classes which are used for the qualitative or quantitative determination of chemical elements and compounds (inorganic and organic) and also for the separation, concentration, masking, and other auxiliary or preliminary operations preceding and accompanying the determination of substances by any methods.[31,32]

We shall consider several principal concepts characterising the properties of the OR and their metal complexes.

1. Contrast

Contrast is one of the important characteristics of a colour reaction, although this term has not been accurately defined in analytical chemistry and it is sometimes confused with reaction sensitivity. The reaction is said to exhibit contrast when two solutions, one of which contains the OR and the other the product of the analytical reaction, differ significantly in their colour under identical conditions.

A quantitative characteristic of the contrast of a colour reaction is the difference $\Delta\lambda$ (in nanometres) between the band maxima in the absorption spectra of the reaction product (MR) and the reagent (R): $\Delta\lambda = \lambda^{MR}_{max} - \lambda^{R}_{max}$. It is assumed that the reaction exhibits a low contrast if $\Delta\lambda < 40$ nm, a moderate contrast if $\Delta\lambda = 40-80$ nm, and a high contrast if

$\Delta\lambda > 80$ nm. It is also necessary to take into account the shape of the spectrum, in particular the half-widths of the absorption bands. If the absorption spectrum of the reaction product has two maxima, then $\Delta\lambda$ is usually calculated from the positions of the band maxima in the absorption spectra of the OR and the complex differing to the greatest extent. The presence of two maxima is characteristic, for example, of the OR of the arsenazo III group.

There are several possibilities for increasing the contrast of colour reactions. It is known that contrast for a reagent of the type of ROH can be enhanced by selecting a solvent promoting the elimination of a proton from the hydroxy-groups. Such solvents can be dimethylformamide (DMF) and dimethyl sulphoxide (DMSO), which are fairly strong proton-accepting solvents. This procedure is used, for example, to increase the contrast of the reactions of phenylfluorone and its analogues.[33]

A second way of increasing the contrast of colour reactions involves the change in the structure of the OR itself—in the simplest case the introduction of suitable substituents into the OR molecule. Usually these are electronegative groups: NO_2, Cl, Br. Alizarin S and many monoazo-compounds containing the oo'-dioxyazo-group, exhibit an increase in the contrast of their reactions with the elements after the introduction of the NO_2 group.

The problem of finding new OR giving rise to contrasting reactions with the elements is more difficult and has been less thoroughly investigated. In order to solve the problem of predicting the contrast of reactions, it is necessary to find the relation between the structural and analytical spectroscopic characteristics of the reagents and their complexes with the elements. The principal difficulty in the solution of this problem consists in the lack of a clear-cut mathematical definition of the characteristics of the contrast and also of the sensitivity, selectivity, and other analytical characteristics of colour reactions. The search for new or more promising OR is therefore at present prosecuted as a rule by comparing the properties of the OR of one or several chemical classes. An example is provided by the procedure whereby the contrast of the colour reactions of OR of the group of arsenazo III can be increased. By varying the substituents in the benzene rings, while retaining the main carbon skeleton of the OR molecule, it has been possible to synthesise more than 100 new OR; some of these are characterised by a very high contrast of their colour reactions.[20] For example, Dicarboxybenzene C, containing two carboxy-groups in the *ortho*-position relative to the azo-group, gives rise to colour reactions with copper ($\Delta\lambda$ = 106 nm) and manganese ($\Delta\lambda$ = 180 nm) in experiments in aqueous organic media (solutions in acetone and propanol). In order to achieve a high contrast, two factors are used in both cases: the choice of the optimum structure of the reagent and the application of non-aqueous solvents.[34]

In order to increase the contrast of colour reactions (and also in order to improve other analytical characteristics), one employs the procedure in which the elements are determined when they form part of the composition of heteroligand and heterometal complexes, which will be discussed in greater detail below.

2. Sensitivity

A series of procedures have been proposed for the quantitative expression of the sensitivity of colour reactions.[35,36] The most universal characteristic of the sensitivity is apparently the molar extinction coefficient ε† of the analytical reaction product. It is usually assumed that, when $\varepsilon < 2 \times 10^4$, the reaction is relatively insensitive, when ε reaches $(2-6) \times 10^4$ it exhibits a moderate sensitivity, and, when $\varepsilon > 6 \times 10^4$, the sensitivity is high. There exists a limiting value of ε ($\sim 2 \times 10^5$). Although reactions with $\varepsilon > 2 \times 10^5$ are known, these are as a rule cascade reactions.

The "apparent" (or average) molar extinction coefficient is a criterion of the sensitivity of the reaction. It is calculated from the familiar formula $\varepsilon = A/cl$, where A is the optical density of the solution to be analysed, c the concentration of the substance to be determined, and l the thickness of the solution for which photometric measurements are to be made. The conditions in the determination of the element are chosen empirically by selecting the pH or masking complex-forming substances which ensure the highest selectivity. One then considers the reaction mechanism, the yield of the coloured compound (which may be less than 100%), the possibility of the formation of ternary or other complexes, and the coexistence in solution of several coloured complexes. Consequently the apparent or average molar extinction coefficient characterises the sensitivity of the analytical method and its comparison with the true molar extinction coefficients provides an idea about the extent to which the sensitivity of the method of determination is reduced compared with the sensitivity of the reaction itself.

We shall consider the possible ways of increasing the sensitivity, drawing a distinction between the sensitivity of the analytical method and the sensitivity of the reaction itself. The sensitivity of the method can be increased by concentrating the element to be determined (for example, by extraction with organic solvents) or by increasing the thickness of the solution for which photometric measurements are to be made. In the method of spot tests there exist procedures whereby one can reduce by 1–2 orders of magnitude the limit of detection of absolute amounts of the test substances;[22] this also applies to the micromethods for the quantitative determination of substances.[4]

The sensitivity of the reaction depends in the first place on the properties of the OR and on the molar extinction coefficient of the reaction products. The reaction conditions (pH, the nature of the solvent, temperature, etc.) as a rule have an insignificant influence on the sensitivity of the reaction and determine only the yield of the reaction product, which is only rarely below 70–80% under the selected optimum conditions of the determination. Nevertheless it is well known that the character of the spectral curve (the position of the maximum and the intensity and half-width of the absorption band) can change following a change in the reaction conditions (pH and the solvent). This is due to the change in the character of the interaction of the OR with the metal: under new conditions, complexes having a different composition or structure are produced. For example, four different reaction mechanisms, which operate depending on the reaction conditions have been established for certain azo-dye reagents.[37] Application of the knowledge of these mechanisms combined with the appropriate alteration of the reaction conditions lead to one of the ways of increasing the sensitivity of the colour reaction.

3. Selectivity

The concepts of the specificity and selectivity of colour reactions have been examined in a number of studies.[38–41] By the term "selectivity of an organic reagent", we understand the range of the reactive components of the mixture to be analysed which can in principle interact with the given OR, giving rise to a colour reaction; by the term "reaction selectivity" we shall understand the range of the elements interacting with the given OR under certain conditions.

†Here and henceforth the coefficients ε are expressed in litre mol^{-1} cm^{-1}.

Methods for increasing the reaction selectivity are known. In the first place they involve the variation of the pH of the medium. In conformity with the theory of analogies,[42] colour reactions in acid media with oxygen-containing OR of the type of ROH are undergone only by elements whose cations exhibit an extremely high tendency towards hydrolysis: B, Pa, Nb, Zr, Hf, U(IV), Pu(IV), Th; apart from the elements already enumerated, colour reactions are undergone also by Al, Ga, UO_2^{2+}, PuO_2^{2+}, and Sc in moderately acid solutions, by the lanthanides, VO^{2+}, Mo, and Cu in weakly acid and neutral solutions, and by Zn, Ba, Sr, Ca, and Mg in alkaline solutions. The optimum (as regards selectivity) reaction conditions are determined by the nature of the OR and other factors, and in most cases the determination of readily hydrolysable elements in strongly acid media is more selective. Thus, allowance for the nature of the ions of the element constitutes an important factor in increasing the reaction selectivity.

Another universal method for increasing the selectivity of the determination involves the application of various masking substances, including complexones.[10,17] It is noteworthy that there is also a possibility of a scheme in which the element to be determined is masked. By measuring the optical densities of the solution before and after adding the masking substances, one can estimate the interference due to the presence of other elements (for example, UO_2^{2+} is masked by potassium hexametaphosphate in its determination with an OR of the arsenazo type).[20]

A promising method for increasing selectivity, which in due course may become universal, involves the determination of the element present as part of the composition of a mixed ligand complex. The number of publications concerning the development of this application has been increasing rapidly; we shall note only one of the latest monographs.[9]

The selectivity of the determination of an element can be increased by employing extraction-photometric schemes. Here one is not dealing with preliminary extraction and subsequent determination of the element but with the employment of the OR simultaneously for extraction and for photometric measurements. The method, which it has been possible to extend to virtually all OR of different classes, even those which are readily soluble in water, consists in extracting the diphenylguanidinium salt of the corresponding inner complex by butyl or pentyl alcohol with subsequent photometric measurements on the extract without any additional operations.[43,44]

The selectivity of the OR is determined by its structure and the nature of the functional-analytical group. Since the number of the possible functional groups is limited (approximately 100 groups have been described and investigated fairly adequately), much attention has been devoted to increasing the selectivity of OR with a specific group. Thus it has been observed[45,46] that the most general method of increasing the selectivity involves the introduction into the molecule of the reagent of substituents, generating steric hindrance to the formation of a complex, in the vicinity of the chelating centre. It has been noted[46] that the principal cause of the difficulty in achieving a high selectivity for the OR is the ability of metal ions to "become adapted" to the coordination requirements of the ligands. The Schwarzenbach principle (the maximum satisfaction of the coordination requirements of the given ion) is therefore inadequate and it is necessary to impose additional conditions for structural correspondence. As an alternative, the principle of at least the minimum satisfaction of the geometrical and donor–acceptor requirements of one ion combined with the maximum possible satisfaction of such requirements for all the other metal ions has been put forward.[47]

One of the most interesting and very promising procedures for achieving a high selectivity or even specificity of the reaction is the application of macrocyclic reagents in the cavities of which can accommodate only ions with specific coordination possibilities (see, for example, West[45]). An improvement of the selectivity of the OR can be achieved also by introducing into its molecule a second complex-forming group together with the main functional-analytical group.[48,49] An even more promising procedure for the creation of selective OR involves the synthesis of reagents with heterocyclic rings containing S, P, N, and other atoms.

For example, rhodanine was proposed at one time for the precipitation of Ag, Hg, Au, and other elements. However, the low solubility of rhodanine and of the products of its interaction with the elements and the low sensitivity of the reactions precluded its wide-scale employment in photometry. At the same time, by virtue of the enhanced reactivity of its methylene group, rhodanine reacts with compounds of different classes—aldehydes, ketones, and diazo-compounds, which has served as the basis for the synthesis of a series of new OR containing chromophoric groups. For example, 5-azo- and 5-condensed derivatives of rhodanine, its five-membered analogues (thiorhodanine, thiohydantoin, selenoisorhodanine, and 3-aminorhodanine), *N*-substituted 3-aminorhodanine derivatives, and the six-membered analogue thiopropiorhodanine, have been synthesised and investigated.[50–52] In terms of sensitivity and contrast, the azo-derivatives and condensed derivatives of rhodanine and its analogues are greatly superior to rhodanine itself. The most valuable analytical reagents proved to be azo-compounds containing aminosulphophenols as the diazo-components. In contrast to the condensed derivatives, the azo-compounds are more soluble and more stable in highly acid media. As a rule, these OR also give rise to more sensitive and contrasting colour reactions with the elements, in particular with the noble metals.

An appreciable excess of alkali, alkaline earth, and nonferrous metals does not interfere with the determination of the noble metals. It is possible to determine one element of the platinum group in the presence of others. This is achieved because of the difference between the optimum conditions for their determination (concentration, nature of the acid, and temperature) and especially by virtue of the different kinetic activities of different complexes of the noble metals, which depend on the nature of the ligands and on the oxidation state of the central atom in the initial complexes. Table 1 presents the conditions in the reactions and their sensitivities for two of the most interesting OR of this series.

Yet another way of increasing the selectivity of analytical reactions, unrelated to the change in the chemical structure of the OR molecule, is based on the use of its different tautomers.

Thus there exist fairly numerous ways of increasing the selectivity of colour reactions, some of which are fairly promising. At the same time there is as yet no universal criterion which would unambiguously indicate the procedure for the specific synthesis of OR specific for each element.

In conclusion of this section, we shall quote several examples of the spectrophotometric determination of anions using OR. Carminic acid ($\varepsilon = 5.7 \times 10^3$), dianthrimide ($\varepsilon = 1.8 \times 10^4$), and alizarin S (sensitivity 0.02 $\mu g\ ml^{-1}$) are most frequently used to determine boron.[53] The reagent dibromoarsenazo II makes it possible to determine boron in 85% sulphuric acid. The reaction exhibits an appreciable contrast ($\Delta\lambda = 110$ nm), sensitivity (0.01 $\mu g\ ml^{-1}$), and selectivity.[54]

OR belonging to the group of 2,7-bisazo-substituted chromotropic acid derivatives (indirect method) are most promising for the determination of sulphate ions.[21] The determination is carried out by a reaction involving the masking by sulphates of highly sensitive colour reactions between barium and the above OR. Among the numerous OR investigated, Orthanilic K has been recommended for the photometric and titrimetric determination of sulphates. In the photometric version it makes it possible to determine sulphate ions in the concentration range 0.03–1.5 μg ml^{-1}. The determination is carried out at pH 4 in 60% acetone or alcohol.[55] Analytical methods for a wide variety of materials have been developed and successfully employed: natural and industrial waters, air and gases, electrolytes, soils, mineral rocks, etc. The reaction is highly sensitive in relation to phosphate, arsenate, thiosulphate, and fluoride ions.

Table 1. The colour reactions of some platinum elements.[50–52]

Element	Reaction conditions	$10^{-4}\varepsilon$
Reactions of sulphochlorophenolazorhodanine		
Pt	3 *M* HCl	3.2
Pt	2 *M* H_3PO_4 + 2 *M* H_2SO_4	10
Rh	14 *M* H_2SO_4 + 6 *M* CH_3COOH	3.5
Ir	10 *M* H_2SO_4 + 6 *M* CH_3COOH	4
Pd	5 *M* H_2SO_4 + 8 *M* H_3PO_4	12
Au	1 *M* HCl	5.2
Ag	pH 8–10	2
Reactions of sulphochlorophenolazothiopropiorhodanine (thiorhodanine)		
Pt	5 *M* H_3PO_4 + 2 *M* CH_3COOH	6.5
Au	3 *M* H_2SO_4 + 3.5 *M* CH_3COOH	2.5
Ag	10 *M* CH_3COOH + 1 *M* H_3PO_4	5.3

Potentiometric methods with ion-selective electrodes and photometric determinations with OR are used nowadays to determine fluorides. In photometry the indirect methods for the determination of fluorides have been almost completely displaced by the direct determination of fluorides in the form of a three-component compound. It has been found that fluorides can be determined by reactions with zirconium and one of the reagents: arsenazo III, Sulphochlorophenol S,[56,57] Xylenol Orange, or Methylthymol Blue.[58] The difference between the rates of the reactions with the reagent of different forms of zirconium (complex fluoride and hydroxide) is used to determine fluoride ions. A direct linear dependence of the optical density of the solution on the fluorine concentration has been observed in the range 0.01–0.32 μg ml^{-1} for Xylenol Orange, 0.01–0.1 μg ml^{-1} for Chlorosulphophenol C, and 0.02–1.4 μg ml^{-1} for arsenazo III.[57,58]

Phosphates are in most cases determined by means of the formation reactions of reduced heteropolyacids. However, the possibility of the formation of different forms of heteropolyacids can lead to non-reproducible results; the selectivity of the reaction is low and so is its sensitivity: $\varepsilon = (2.1–2.7) \times 10^4$. The reaction with iron(III) ions in the presence of dithizon has been suggested for the determination of phosphorus (in the form of PO_4^{3-}).[59]

III. NEW METHODS FOR INCREASING THE EFFICIENCY OF SPECTROPHOTOMETRIC ANALYSIS

It is possible to differentiate at least three procedures for increasing the efficiency of the known analytical reactions: (1) the use of reactions involving the formation of multicomponent complexes; (2) the application of non-aqueous and mixed solvents as the reaction medium; (3) the use of surfactants in different versions of the reactions. These procedures refer to both colour and luminescence reactions and sometimes make it possible to increase the sensitivity by an order of magnitude and above, to shift the selectivity in the required direction, to improve the reliability of the analysis, etc.

1. Mixed-Ligand Complex Formation

Mixed-ligand complex formation, i.e. the transition from binary to more complex complexes containing three and more components, makes it possible to improve almost all the analytical characteristics of colour reactions. This method has been widely incorporated in practical chemical analysis from the 1950's onwards and has continued to develop.[9,60]

The importance of heteroligand complexes for analytical chemistry is due to their great variety, since mixed-ligand complexes constitute the most probable form in which ions exist in solution. All these equations have been discussed in detail in a monograph.[9] Heteroligand complexes are widely used in extraction–photometric analytical methods. Compounds of organic cations with metallochromic chelates constitute the most common group of compounds in the acid dye–metal ion–organic base systems. The role of the cations in such compounds reduces to neutralising the excess negative charges on the OR due to the presence of sulphogroups[45,61] or dissociated hydroxy-groups, which are not involved in chelate formation.[62,63] Analysis of the literature data has shown that more than 40 dyes are employed as metallochromic indicators, approximately 20 organic cations are used to neutralise the excess charges, and methods are available for the determination of more than 30 metal ions.[15,18,24,64,65]

Methods have been developed for the photometric determination of metals in the form of complexes with metallochromic reagents involving the introduction of quaternary ammonium salts into such systems.[9] The contrast of the reactions increases significantly in this instance. The use of four-component and more complex mixtures leads to new possibilities for the development of photometric and extraction-photometric analytical methods.

2. Organic Solvents in Photometry

One of the new methodological procedures in photometry, which makes it possible to improve the analytical characteristics of the known reactions and also to discover new reactions, involves the employment of organic solvents which not only constitute the medium for the photometric reactions but also influence significantly the reaction mechanism. The effects observed in photometry on passing from aqueous to aqueous organic or organic media are extremely varied. The sensitivity and contrast of the colour reactions and the rate of development of the colour increase, the composition of the complexes changes, and the complexes of elements in a particular oxidation state are stabilised. The observed wide variety of effects is due to the complexity of the processes

influencing the complex formation. Solvents displace tautomeric and acid–base equilibria involving OR, solvate in different ways both the reactants and the reaction products, alter the dielectric constant of the medium and the structure of the solutions, and influence the steric configuration of the complexes.

The application of organic solvents in photometry makes it possible to extend greatly the range of OR and masking complex-forming compounds. Solvents which are most readily available and are most miscible with water are usually employed in spectrophotometry: alcohols, acetone, dioxan, carboxylic acids, DMSO, and DMF. Studies have been made of the influence of solvents on the colour reactions of the elements with OR of different classes: with azo-compounds based on heterocyclic amines,[66,67] formazans,[68,69] and compounds of the triphenylmethane series.[70]

The influence of solvents on the reactions of the elements with 2,7-bisazo-substituted chromotropic acids and also with reagents of the triphenylmethane series has been investigated in detail.[71] A sharp increase of the sensitivity of the colour reactions of Ca, Sr, and Ba with OR belonging to the class of 2,7-bisazo-substituted chromotropic acids has been observed in aqueous acetone and aqueous propanol media.[71] Thus highly sensitive colour reactions of Sr and Ba with carboxynitrazo have been observed in water–acetone mixtures containing 40 and 80 vol.% of acetone respectively ($\varepsilon \cong 1.4 \times 10^5$, $\Delta\lambda > 180$ nm for both reactions),[72] while in a mixture containing 75 vol.% of acetone the reaction of Ca with Methanilic C takes place ($\varepsilon = 0.9 \times 10^5$, $\Delta\lambda \cong 110$ nm).[73] In acetone (containing less than 5 vol.% of water) and in propanol (<0.5 vol.% of water) there is a possibility of sensitive colour reactions for Ni, Co, Mn(II), and Cu.[74] Some of them, for example the reactions with carboxybenzene [Carboxybenzene S?] are characterised by a high sensitivity and contrast ($\varepsilon \cong 1.6 \times 10^5$, $\Delta\lambda > 180$ nm).

In aqueous organic media containing acetic acid, a sharp increase of the sensitivity and contrast of the colour reactions of Al, Be, Ga, and Ti with OR based on *c*-aminohydroxyphenols has been observed.[75] In the presence of H_3PO_4 and H_2O_2, aluminium and titanium form respectively ternary complexes which are not characteristic of other elements; there is a sharp increase of the rate of development of colour. The increase of the sensitivity and contrast of the colour reactions of Be with Chrome Azurol S has been observed in water–propanol mixtures.[76]

The increase of selectivity is determined both by the properties of the solvents (mainly their solvating capacity) and by the new possibilities for masking. For example, in acetic acid media the range of elements capable of giving rise to colour reactions is much more limited than in other solvents, which itself increases the selectivity. This may be associated with the fact that many elements form stable acetates, which entails the loss of the possibility of their interaction with the OR. For example, the selectivity of the colour reactions used to determine Be, Al, and Ti can be sharply increased by employing hydrogen halides (HF, HBr, HCl) as masking-complex-forming agents, which bind many interfering elements (In, Hg, and others) in anionic halide complexes and at the same time do not interfere with the reactions of Be, Al, and Ti. As a result, it is possible to determine Al, Be, and Ti in the presence of a more than 2000-fold excess of Ga, In, Zn, Bi, and other elements.[77,78]

The colour reactions of alkaline earth metals with OR belonging to the Orthanilic, Anthranilic and Benzene group in aqueous organic media are selectively masked by certain anions. Thus in aqueous organic media the sulphates selectively mask the colour reactions of Ba and Sr with Methanilic S, while oxalates mask the reactions of Sr with carboxynitrazo, which makes it possible to determine Ca in the presence of Ba and also Sr in the presence of Ca.[72] A difference in the masking of the colour reactions of Be and Al with Chrome Azurol S is observed in aqueous propanol media, which makes it possible to determine Be in the presence of Al.[76]

Highly sensitive reactions of Ni and Mn(II) with Carboxybenzene C or of Ti with nitrobenzene have been used to determine these elements in chloroform extract after the extraction of nickel by dimethylglyoxime,[79] of manganese by diethyldithiocarbamate,[80] and of titanium by cupferron.[81] The examples quoted by no means exhaust all the possibilities for the improvement of the analytical characteristics of the colour reactions using organic and aqueous organic media.

3. Application of Surfactants

The use of surfactants in photometric analysis is not a new application, but the most interesting results, both practical and theoretical, have been obtained only in recent years. The use of long-chain ammonium and pyridinium bases, namely cetyltrimethylammonium,[82] cetylpyridinium,[83] Zephiramine,[84] and poly-hydroxyethylated ethers of alkylphenols[85] had been described earlier. Water-soluble ionogenic and non-ionogenic surfactants are most suitable for analysis.

The salts of aliphatic primary, secondary, and tertiary amines, quaternary ammonium bases, alkylpyridinium, and a number of other nitrogen-containing bases such as imidazoline, imidazole, pyrimidine, oxazoline, and others behave as cationic surfactants. Cationic surfactants such as sulphonium, phosphonium, and thiuronium compounds are known. Alkanesulphonates, alkylarenesulphonates, alkyl sulphates, and related compounds containing additional polar groups (carbamide, ester, etc.) in the chain behaves as anionic surfactants.

Hydroxyethylated aliphatic acids, glycerol esters of stearic acid, esters of triethanolamine with organic acids and alkylphenols, hydroxyethylated high-molecular-weight alcohols, block-copolymers of epoxypropane and ethylene, polyethylene derivatives of alcohols, poly(ethylene glycol) derivatives of acid amides, amines, epoxypropane, etc. belong to the group of non-ionogenic surfactants.

The introduction of cationic surfactants, particularly those containing a quaternary nitrogen atom and the cetyl group, into a metal ion–OR system (at the appropriate pH) leads to a sharp increase of the contrast and sensitivity of the reactions. Highly effective methods have been developed for the determination of Be, Sc, Y, the lanthanides, Al, Ga, In, Ti, Zr, V, Nb, Ta, Mo, W, Mn, Fe, Co, Ni, Cu, Zn, Ge, Sn, Bi, Th, U, and other elements.[86–91]

Another analytical application of surfactants involves the determination of the percentage content of the OR in their preparations. The method is based on the formation of blue ionic associated species, basic triarylmethane dyes, and anionic surfactants.

Questions concerning the theory of these reactions, which are of interest for analytical purposes, have been discussed in the literature.[88–93] The mechanisms of the interaction of different types of surfactants are different. For example, it has been established that cationic surfactants and OR of the type of Catechol Violet react at a surfactant concentration below the critical concentration for micelle formation.[89–91] It has been suggested that compounds of the type of ionic associated species are produced. However, a sharp change in the colour of the solution indicates the interaction of the cationic surfactant via the hydroxy- and carboxy-groups and not via the sulpho-groups of the OR molecule. Thus the role of the surfactants reduces to exerting an additional influence on the π-electron system of the OR by forming an associated species via the oxygen of the free hydroxy-group, which entails a bathochromic shift of the long-wavelength absorption band.

A somewhat different picture is observed on formation of chelates of phenol-carboxylic acids of the triphenylmethane series. In the absence of surfactants, the formation of metal complexes via the carboxy-groups is characteristic of these OR.[94] The addition of cationic surfactants leads to the blocking of the carboxy-groups owing to the formation of associated species and to the transformation of phenolcarboxylic acids from polyfunctional OR to monofunctional OR, because only one complex-forming group, containing the phenolic hydroxyl and the carbonyl oxygen atom of the COOH group in the o-position relative to the hydroxyl remains available. Consequently the role of surfactants in relation to phenolcarboxylic acids of the triphenylmethane series presumably does not reduce solely to influencing the π-electron system of the OR; the character of the coordination of the metal atom also changes in the presence of the surfactant. The appearance of a narrow well resolved absorption band and the high extinction coefficient of the complex are determined by the characteristics of the structure of the first coordination sphere of the metal. The strong polarising action of the metal, the asymmetry of the OR molecule, and other features of the electronic structure of the complex are apparently of decisive importance.

When non-ionogenic surfactants are used, the mechanisms of their reactions with OR as well as with the complexes produced are somewhat different. The corresponding colour reactions are observed only after the attainment of the critical concentration for micelle formation with the surfactant, i.e. the corresponding processes probably take place in the micellar phase.[92-99] Such processes, involving the displacement of the equilibrium as a result of the local concentration of substances on the surface of the micelles, are known and have been combined under the term "micellar catalysis".

The use of surfactants in combination with OR is an example of the fact that the analytical possibilities are far from being exhausted even as regards well known reagents and the application of new ideas from related branches of science can significantly improve the principal analytical characteristics of large classes of OR.

We may note that significant advances in the development of the theory of all three principal methodological procedures (the use of heteroligand and heterometal complexes, non-aqueous solvents, and surfactants in spectrophotometry) already make it possible to carry out experiments designed to improve these methods in a purposeful manner and not at random and unsystematically. This is also promoted by the fact that the principal elements of the theories of all three methodological procedures have a single physicochemical basis—comprising vigorously developing ideas concerning surface and solvation effects, phenomena associated with hydrophobic hydration, structure formation in the solvents, and the influence of these phenomena on the tautomeric and acid–base equilibria involving the OR and ultimately on the mechanisms of the complex-formation reactions.[90,91,94,100]

IV. THE CHOICE OF ORGANIC REAGENTS FOR THE DETERMINATION OF INDIVIDUAL ELEMENTS

By virtue of the advances in their synthesis, the number of OR proposed for the determination of individual elements has continuously increased and has already reached several thousands. The principal difficulty facing the analytical chemist is not the search for OR for the determination of a particular element but the selection of the best OR among many others. It is not always clear from the literature whether a newly described compound is the most effective OR for the given ion or whether the author investigated the given compound together with others, which are frequently analogues of a known OR, in order to obtain a more complete picture of the interaction of OR having similar structures with metal ions. Much attention has therefore been devoted in recent years to studies designed to obtain comparative analytical data characterising the efficacy of various OR in the determination of individual elements.

The principal characteristics which must constitute the basis of the selection of the reagents are (1) sensitivity, which can be expressed in terms of the molar extinction coefficient or with the aid of other parameters, (2) stability of the reaction product expressed in terms of the stability constant, (3) the limiting dilution or the observation limit, which are associated with the above two quantities, (4) selectivity with respect to anions, and (5) the pH necessary for the maximum yield of the complex (as a rule the more valuable OR make it possible to determine the elements in a more acid medium). The contrast of the colour reactions $\Delta\lambda$, the influence of the reagent (as the background substance) at the optimum (working) wavelength ($\varepsilon_{MR} - \varepsilon_R$ or $\varepsilon_{MR}/\varepsilon_R$ at λ_{opt}), the selectivity in relation to cations, and also the rate of equilibration, the stability of the OR and the reaction product with respect to the action of oxidants, reductants, and other external influences, the extractability of the complex, etc. are no less important characteristics.

Table 2. Examples of group reagents for the photometric and extraction-photometric determination of the elements.

Reagent	Elements
Chrome Azurol S	Be, Al, Ga, Zr, Th, Fe, V, Cu, Mn, Sn, Ti
Antipyrine C	Be, Ca, Cu, Ni, Zn, La, Ge, U(VI), Th, Al, Ga, In, Zr, Sc
Arsenazo I	U, Th, Zr, Sc, Ln, Al, Be, Ti, Nb, V, In
Arsenazo III	Th, Zr, Hf, Np, Pu, Pa, U, Sc, Ln, Pd, Ca, Pb
Arsenazo M	Ln, Cu, Pb, Ca, Sr, Th, Ba, Bi, Zr, Hf, Mg, Al, Zn, Cd, Ga, In, Mn, Ni, Ru, V
Dithizone	Pb, Zr, Cd, Hg, Ag, Cu, Bi, Pd, Mn, Fe, Co, Ni
Sodium diethyldithiocarbamate	Ti, V, Cr, Mo, Mn, Fe, Co, Ni, Cu, Ru, Pd, Ag, Os, Ir, Pt, Au, Tl, Bi
Xylenol Orange	Al, Be, V, Ga, Zr, Fe, Cd, In, Cu, Mo, Nb, Sn, Pd, Pb, Tl, Ti, Th, Bi, U
Methylthymol Blue	Al, V, Ga, Fe, In, Ln, Ca, Mg, Mn, Cu, Ni, Pb, Ti, Th, Zr, Zn
Pyridylazoresorcinol	Nb, Ta, Co, Pd, In, Ga, Ln, Cu, Zn, Cd, Tl, Sc, Th, Pb, Bi, U
Sulphochlorophenol S	Nb, Zr, Sc, Mo, Al, Ga, In, Cu, V
Thoron I	Th, U(IV), Zr, Be, Se, Pu, Np

The selectivity of the OR is one of the most important criteria of its analytical value. However, the number of specific or highly selective OR is extremely limited. The creation for each element of an assortment of OR which mutually supplement one another as regards selectivity has been increasingly considered in studies of recent years. Depending on the assumed content of other interfering elements in the object to be analysed, a specific OR is employed or, if possible, one OR is used for the separation of the element and another for its determination. For example, arsenazo III and Sulphochlorophenol S are mutually complementary OR for the determination of zirconium. Arsenazo III makes it possible to determine zirconium in the presence of niobium, molybdenum, and copper, but thorium, uranium, and the lanthanides greatly interfere with the successful outcome of the analysis. On the other hand, Sulphochlorophenol S makes it possible to determine zirconium in the presence of thorium, uranium, and the lanthanides, whereas the presence of niobium, molybdenum, and copper interferes with the analysis. Such pairs of OR can be selected

from many elements. If the solution to be analysed is complex and contains a wide range of elements or if its composition is not known beforehand, then one of the complementary OR can be employed to isolate the element to be determined (for example, by extracting zirconium together with niobium, molybdenum, and copper) and then zirconium is determined in the extract with arsenazo III; the elements isolated together with zirconium do not then interfere with the analysis.

The creation of an assortment of OR for the determination of each element makes it possible to confine oneself in analytical practice to the wide-scale employment of only some of the OR synthesised–group reagents, each of which is in principle suitable for the determination of several elements. The advantage of using a limited number of group OR in analytical practice is that they can be investigated comprehensively and a rational scheme can be selected for the determination of each element. Table 2 presents some of the most important group OR used for the spectrophotometric determination of the elements as well as the elements with which they can give the most characteristic colour reactions. The creation of a rational assortment of OR for the determination of individual elements constitutes a complex and fairly laborious task, because it is then necessary to take into account numerous factors both scientific and industrial. In the USSR such investigations are being prosecuted by several groups of investigators.[6,7,15,18–21,23–27,29,101–117]

V. DEVELOPMENT OF THE THEORETICAL PRINCIPLES OF THE ACTION OF ORGANIC REAGENTS

The studies which are being carried out on the theory of the action of OR can be as a rule assigned to three classes: (1) the determination of reliable thermodynamic and kinetic characteristics of the processes leading to a specific analytical effect; (2) the study of the mechanism of complex formation, i.e. the determination of the consecutive steps in the formation of the reaction products, and the elucidation of the structures of the OR and the final reaction products under different conditions; (3) direct study of the effect which determines the analytical value of the OR, i.e. the nature of the colour reactions in the case of OR for photometry, luminescence, etc.

The question of the structure of the OR and their complexes with the elements is the basis of all subsequent theoretical constructions associated both with the explanation of the analytical effects of the given OR and with the possibility of predicting to some extent the properties of new OR. Babko noted[16] that the structural formulae of the complexes of the elements, even those with known OR, frequently exist as a "matter of tradition" and have been copied from one communication to another without due justification. This suggests a definite lag in the development of a general theory of the action of OR compared with the advances achieved in the field of their practical application. Indeed, even the determination of the classical structural formula constitutes a non-trivial task for many OR and their metal complexes.

The first investigations of Chugaev, Feigl, Belcher, and Kulberg, some of which have been mentioned in reviews,[32,118] are well known. Alimarin's studies have made a great contribution to the development of ideas about the functional groups in OR and about the relation between the structure and properties of the latter.[119,120] Later Kuznetsov developed a series of theoretical ideas, which explain the analytical action of OR: the range of elements forming complexes with reagents having a given structure (theory of analogies),[42,121] the mechanism of solid-phase colour reactions,[122] and intramolecular dissociation (ionisation).[123,124] The theoretical principles of the extraction-photometric method for the determination of the elements in relation to water-soluble complexes have been developed.[44,125,126]

Subsequent research concerned the investigation and explanation of the mechanism of the analytical action of arsenazo III and its analogues,[127] the theory of colour reactions of hydroxylated azo-compounds,[128,129] the study of acid dissociation[130] and protonation[131] of organic reagents, the determination of the relation between the reaction conditions and the properties of both the OR and the metal cation (the protonation constant of the reagent, the solubility product of the metal hydroxide, and the pH corresponding to 50% reaction),[132] and the determination of four types of colour reactions of organic reagents with elements differing in the structure of the complexes and their spectrochemical properties.[37,132–135] The theory of the action of azo-compounds as indicators has been investigated;[136] the theoretical principles of the employment of aqueous organic solutions as media for colour reactions have been developed;[74,100,137–139] the structure and properties of mixed-ligand complexes have been investigated;[140] atomic models have been used to establish the structure of OR and their complexes;[141] the structures of several complexes have been determined by EPR;[142] a new interpretation of the concept of the functional–analytical group of the OR has been proposed;[143] the kinetics of rapid colour reactions have been studied;[144,145] a theory of the application of surfactants in spectrophotometry has been devised.[86–96]

1. Chemical and Physicochemical Methods for the Determination of the Structures of Reagents and Complexes

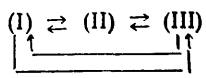
The physicochemical methods for the study of the structure of reagents and inner complexes of the elements with OR (spectrophotometry, EPR, potentiometry, and infrared spectroscopy) make it possible to obtain only indirect information about the structure of the given substance. Direct physical methods (X-ray diffraction analysis) are not applicable in all cases. Perhaps only the NMR method in its various versions, with its ever increasing instrumental capacity, may become in the immediate future a reliable and universal procedure for organic structural analysis.

The structure of the OR and its tautomeric and ionic states in the main determine the complex-formation processes and ultimately the analytical effect of the reaction. The difficulty of establishing the state of the OR and the structure of its separate forms is due to the fact that all the chemical and physical properties of OR are manifested integrally, i.e. can be caused by the simultaneous presence of a series of equilibrium forms.[146] The traditional physicochemical methods, including spectrophotometric methods, cannot always yield the required information. For example, the simplest aromatic azo-compound (azobenzene) has two stereo-forms: *cis*- and *trans*-azobenzenes.[147] These forms differ in their dipole moments and melting points; the steric differences between them have been established by crystallographic investigations. Analogous stereoisomers have been found for a series of substituted azobenzenes and azonaphthalenes.[148] Under specific conditions, one of the ionic and tautomeric forms of the reagent usually predominates. In this case the simultaneous application of spectrophotometric and potentiometric research techniques yields satisfactory results when an attempt is made to establish the sequence of stages in acid ionisation.[149] However, the data obtained must be treated as preliminary.

In general, allowance for tautomers, particularly for azo-compounds as OR, constitutes the most complex problem, which cannot always be solved by classical spectrophotometric

methods for the study of reactions. As an example, we shall consider the OR with the simplest structure—Acid Chrome Dark-Blue.[141,150] It is possible to imagine four equilibrium forms of only one ionic state of this reagent in 0.1 M H_2SO_4: (I), (II), (III), and (IV) (see below).

The existence of the reagent in the sole form (II) has been postulated[150] and the dissociation constant of this particular form has been calculated. The existence of the equilibrium (II) $\rightleftarrows$ (IV) has been postulated in another study[151] under the same conditions. Later quantum-chemical calculations demonstrated[152] that the state of the reagent in 0.1 M H_2SO_4 is described satisfactorily by the following scheme:

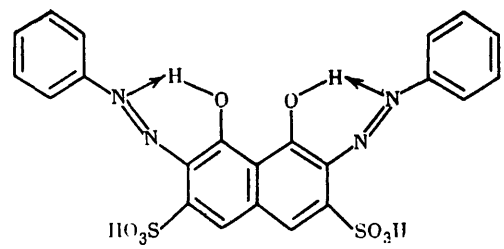


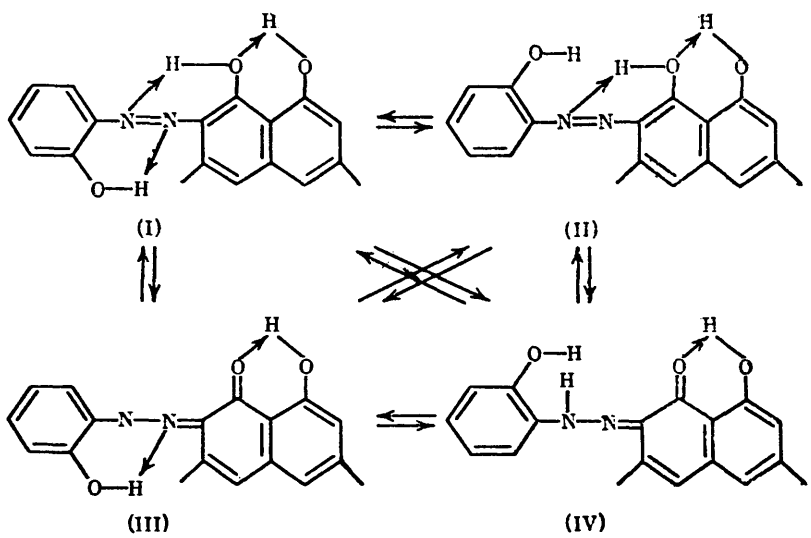
The phenomenon of tautomerism is well known but until recently such processes were considered only in isolated studies.[153,154] It was then usually assumed that the tautomeric equilibrium is almost wholly displaced towards one of the forms. Nevertheless, in determining the state and the characteristics of the reactivity of the OR, it is necessary to demonstrate in the first place the existence of one form or to estimate the concentrations of other forms, which, if they do exist, can interact with metal ions. It is known that the metal does not necessarily interact with the dominant form of the OR present in solution. The presence of metal ions can shift the equilibrium towards the formation of the complex with the form of the OR which would be less stable in the absence of the metal and would be present in solution at a low concentration. All these factors must be borne in mind in interpreting the mechanism of the complex formation reaction.

It is possible to quote a multiplicity of examples of the situation where different investigators have proposed several different structures for the same complex on the basis of the study of the latter by physicochemical methods. Other procedures, developed in recent years, which make it possible to obtain new information about the structure of the complexes and the reaction mechanisms and which have been developed in recent years, are considered below.

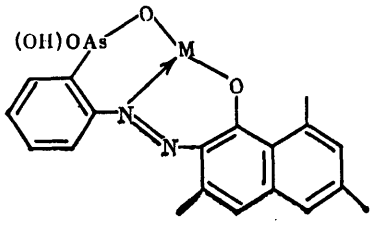
2. The Atomic Model Method

The method of atomic three-dimensional scale models, which has been used for a long time and extensively in theoretical organic chemistry, is in many instances very useful in determining the structure of OR and their complexes. For example, atomic models clearly show that, for OR which are azo-substituted derivatives of chromotropic acid, the only possible planar configuration is the *trans*-configuration of the molecule owing to the steric hindrance by the sulphogroups in the naphthalene nucleus. Thus, for example, the azo-form of the reagent, which is referred to as Benzene S, can be represented only by the following structure:



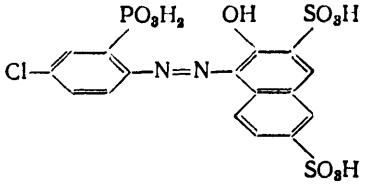


The method of atomic models made it possible to establish that the presence of bulky groups (AsO_3H_2, PO_3H_2, SO_3H, and even COOH) in the organic reagent in the o-position relative to the azo-group precludes the approach of the metal cation to the azo-group in the plane of the OR molecule and the metal ion must therefore be located somewhat above or below the plane of the molecule of the reagent.[141] For example, the structures of complexes of the type



which are usually put forward, are feasible in principle but only under conditions where the planes of the benzene and naphthalene rings have been rotated by ~25–30° and the metal atom is located above the plane of each ring. Only then is the closest contact achieved, within the limits of the sum of the average ionic radii, between the metal atom, on the one hand, and the atoms of the salt-forming groups and the nitrogen atom of the azo-group, on the other.

Three-dimensional atomic models make it possible to establish also other characteristic features of the structure of OR and their complexes. For example, it has been found[141] that, on interaction of a metal ion with chloro-phosphonazo P



the true structure of the complex having the composition MR_2 is one where the two molecules of the above OR are disposed around the metal ion with a coordination number of 6. In this case the molecule has a propeller structure; the planes of the benzene and naphthalene rings are parallel in pairs. In the molecule of the OR the angle between the planes of the two rings is 25–30°; the phosphono-groups are located on top, outside the plane of the benzene and naphthalene rings, while the metal atom is also outside these planes. Analysis of the model showed that another configuration, in which both azo-groups are in the same plane as the metal atom, can also be achieved. The above examples demonstrate the usefulness of the method of atomic models for the preliminary analysis of the possible structures and for deciding whether their existence is in principle possible or impossible.

3. Quantum–Chemical Methods for the Investigation of Colour Reactions

Quantum–chemical methods have been used for approximately 20 years in the study of complex organic reagents with specific features. They led to a way of solving certain important problems in the theory of the action of organic reagents which could not be achieved by the traditional methods available up to that time.[155–159] Thus Hückel's simple version of the quantum–chemical LCAO–MO method makes it possible to calculate the positions of the bands in the absorption spectrum of the OR and to estimate the total π-electronic energy of the system and the relative band intensities. The calculated characteristics of several structures obtained (the positions of the absorption band maxima and their intensities) have been compared with the corresponding experimental data and the structure is selected on this basis.

The LCAO method can also yield additional information about the electronic structure of the molecule of the OR and the complex: about the bond order (the amount of double bond character), about the π-electronic charges on the atoms, and about the free valence indices for individual atoms, i.e. it is possible to formulate the molecular diagram for the OR.

During recent years, extensive data have accumulated as a result of quantum–chemical studies of OR of different classes and their complexes with the elements. Apart from those already mentioned, we may also indicate several novel communications,[160–164] reviews, and monographs.[20,26,165] In the present review we would like to mention only certain features of the application of quantum–chemical methods, their scope, and the prospects for their further applications.

The structural complexity of many OR, the presence of several functional–analytical groups, and the possibility of tautomeric transformations and geometrical isomerism make the task of investigating the mechanism of the complex formation reaction and of the nature of the colour reactions extremely difficult. In calculations of the electronic and energetic characteristics of both the OR and the complexes, one therefore begins with a simplified model of these compounds. Since the S, As, and P atoms forming part of the acid groups SO_3H, AsO_3H_2, PO_3H_2, and other similar groups do not possess an unshared electron pair, their π-electron systems can be assumed to be isolated and to be virtually uninvolved in conjugation. The influence of such groups can be regarded as a perturbation, which alters the Coulombic integral of the carbon atom adjoining the group, as suggested by Wheland and Pauling.[166] The parameters of the heteroatom necessary for this purpose are calculated by Rasch's method;[167] the overlap integrals are found from tables;[168,169] the ionisation potentials are taken from Vedeneev's handbook,[170] the effective charges are calculated in accordance with Slater's rule,[171] and the interatomic distances are taken from tables.[172] The heteroatoms incorporated in the π-electron system are taken into account by introducing semiempirical parameters for the Coulombic and resonance integrals.[26]

At the present time the task which is to be performed by means of the quantum–chemical theory of the structure and action of OR is fairly limited. In the first place, it is necessary to understand the nature of many of the factors already known, for example the influence of the type of substituents, their positions, etc. Using the data obtained, it is possible to formulate certain hypotheses concerning the alteration of the structure of the given OR, which can lead to the required change in its properties: an increase in the sensitivity, selectivity, and contrast of the reaction, in the stability of the complex, etc. New OR, whose analytical value is then tested in practice, are synthesised on the basis of these postulates.

We shall consider the question of the problems of interest for the study of OR which can be actually solved by the computational methods of the quantum–chemical theory of polyatomic molecules. The most common computational method is the self-consistent field method or the Hartree–Fock–Roothaan method, which can lead to the solution of an extremely large number of problems of practical importance

when account is taken of correlation effects.[26,173,180] In calculations on polyatomic molecules mathematical difficulties arise and investigators are forced to introduce approximations of various kinds and to abandon rigorous versions of the theory in favour of semiempirical ones.[174]

Such methods are even more complex than, for example, the Hückel or the Pariser–Parr–Pople methods and their application requires a large amount of computer time; however, the development of computers makes their large-scale application feasible.

We shall consider certain conclusions which can be reached on the basis of the experience already gained in employing quantum–chemical methods for the solution of various problems associated with the structure and properties of OR. One of the first problems in the theory of OR whose solution by quantum–chemical methods has begun involves the explanation of their colour and the causes of its change on complex formation. One may say that this problem is one of the most important and, moreover, it can be best solved using quantum-chemical methods. The vast majority of OR have an extensive conjugation system and the long-wavelength bands in the spectrum are associated with the $\pi-\pi$ transitions (transitions between states of delocalised electrons)–this makes it possible to employ effectively various methods based on the π-electron approximation. The Pariser–Parr–Pople method, which, when combined with configuration superposition methods, makes it possible to simplify the problem of selecting the parameters and to carry out calculations not only for singlet but also for triplet excited states, is preferable for the calculation of the electronic spectrum.[173] As a result, it is possible to include in the investigation also luminescence spectra, which is an extremely promising feature of the analytical application of OR. The Hückel method is in principle inapplicable for this purpose.

The main difficulty in the calculations of the electronic spectra consists in the fact that, since a semiempirical method is used, it is necessary to select a system of initial parameters which would describe satisfactorily not only the spectrum of the given OR (this is not difficult to do) but would also be capable of being transferred to molecules of a specific class, which would lead to the possibility of predicting the spectroscopic properties of a large group of reagents.

By carrying out the appropriate calculations for both OR and for the complex, it is possible to find a way whereby new reagents can be sought. The construction of schemes relating the positions of the long-wavelength absorption band to the site at which the substituent is introduced in the OR molecule is useful in this connection. Examples of such schemes can be found in the literature.[174]

Using this kind of approach and comparing the wave functions for the highest occupied and lowest unoccupied orbitals of the molecules of isomeric phenolazonaphthols, Pilipenko et al.[175] concluded that the azo-derivatives of 1-naphthol should give rise to a more contrasting reaction than the azo-derivatives of 2-naphthol. The reagents synthesised confirm the above hypothesis. Theoretical analysis also led to the conclusion that the contrast of the reactions can be increased by introducing substituents into the aromatic nuclei of OR molecules and that it is useful to employ substituents which exert only an inductive influence. This led to the synthesis of an OR, namely Picramine Epsilon, whose reaction with zirconium and copper is twice as sensitive as that of Picramine P used for this purpose hitherto.[176]

Quantum–chemical calculations helped to demonstrate the likely usefulness of the synthesis of new OR containing the *oo'*-aminohydroxyazo-group and the *oo'*-carboxyaminoazo-group. These OR proved to be extremely sensitive and selective in reactions with palladium, rhodium, molybdenum, and platinum.[177] *N*-Methylanabasine-α-azo-4-cyclohexylresorcinol has been synthesised on the basis of a preliminary calculation for the photometric determination of indium.[178]

Together with the study of spectroscopic properties, quantum methods have also proved useful for other purposes. They can be used, for example, to study charge transfer in oxidation-reduction reactions. Thus, quantum–chemical studies of the electronic structures of OR as a function of the character of the substituent, resulted in the specific synthesis of new reagents: 4-arsono- and 4-phosphonophenylanthranilic acids, phosphonodiphenylamine, and diphosphonodiphenylamine, which are effective oxidation-reduction reagents for the determination of iron, chromium, and vanadium.[179]

There are as yet few examples of the specific synthesis of OR, but one should note that the number of special quantum–chemical studies whose aim is to predict new reagents is also still very small. The limited number of examples of this kind arises mainly due to the fact that analytical chemists have made little use in their investigations of quantum–chemical computational methods, particularly those where account is taken of all the valence electrons, such as CNDO, INDO, and especially MINDO/3.[180]

Attention must be drawn to the great benefit which theoretical analytical chemistry can derive from the application, together with the usual language of structural formulae, of the language of molecular diagrams based on concepts of fractional atomic charges and fractional orders. Numerous examples have shown that molecular diagrams in many respects promote the elucidation of analytical reactions. It is also significant that such molecular diagrams change comparatively little when more complex methods for their calculation are resorted to.

4. Conformational Analysis

The most important characteristic of OR and their complexes which can be successfully investigated by means of modern theoretical chemistry is the geometry of the systems. The study of geometrical parameters is particularly important, because the cause of complex formation reactions and the spectroscopic properties of complex molecules are in many respects determined by their shape and geometry.

Molecular geometry can be determined by theoretical conformational analysis based on the approximation of atom–atom pair potentials. This method, which has been examined in monographs,[181,182] is used widely to investigate the most varied organic compounds, including large biological systems. In almost all cases where it was possible to compare the results of such conformational calculations with experimental data or with the results obtained via other independent calculations it was found that the method is fairly reliable. This makes it possible to regard it as a procedure with a high predictive power.[183]

The mathematical task reduces to finding the potential energy minimum for the system by varying the interatomic distances. This problem can be solved with the aid of well known mathematical procedures. The simplicity of the expression used for the potential energy makes it possible to formulate the problem formally and to develop special computer programmes distinguished, on the one hand, by great power, and on the other hand, by a great simplicity of the representation of the initial data; this has made the methods of theoretical conformational analysis very accessible.

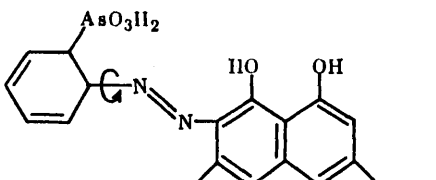
The conformations of a number of organic reagents of the arsenazo III group and related compounds have been calculated[183] and the possibility of rotation about the $C_{Ar}-N$,

N=N, C_{Ar}–AsO_3H_2, C_{Ar}–SO_3H, C_{Ar}–COOH, and C_{Ar}–OH bonds as well as the possibility of the deformation of the valence angles at the nitrogen atoms in the azo-group and the oxygen atom in hydroxy-groups have been examined. Calculations showed that the molecular skeleton of organic reagents without substituents, such as arsenazo III, is planar. The rotation about the C_{Ar}–N bond at the naphthalene nucleus leads to the appearance of stereoisomers differing in the orientation of the azo-group. Regardless of its orientation, all the isomers are energetically equivalent. The substitution of the hydrogen atoms in the 1- and 8-positions in the naphthalene nucleus by hydroxy-groups results in a sharp differentiation of the possible conformers as regards energy: the conformations in which there is a possibility of O–H...N hydrogen bonds are energetically more favourable (approximately by an amount equivalent to the energy of the hydrogen bonds formed) than the conformations in which there are no hydrogen bonds. The formation of conformers containing the O–H...O hydrogen bond (asymmetric conformations) is also possible in principle. All the possible conformations of such molecules are planar.

The presence in a system of this kind of a bulky rotating group results in a sharp increase of the complexity of the picture and renders the principal molecular conformations non-planar. The conformations in which two hydrogen bonds are formed have the lowest energy. At the usual temperatures the equilibrium mixtures can contain only those forms because they are energetically more favourable (the energy gain is 10–20 kcal mol^{-1}).

In order to elucidate the mechanism of the complex formation reaction or to interpret the experimental data for the formation of complexes by azo-reagents with the elements, it is sufficient to know merely the equilibrium geometry of the conformers; it is essential to know how rigid are particular conformations and what is the approximate energy expenditure needed for rotation about the bonds in order to attain the most favourable geometry for the formation of the complex; it is also important to estimate the feasibility of the transition from one conformation to another.

Such calculations for arsenazo I



showed[184] that the rotation about the C_{Ph}–N bond (indicated by an arrow in the schematic diagram above) is fairly free: rotation by ~30° requires an energy expenditure of ~1 kcal mol^{-1}; consequently the OR can readily undergo a change in conformation on complex formation. The barrier to the transition to a neighbouring (relatively unstable) conformation is also low and amounts to 4–5 kcal mol^{-1}.[183,184]

Conformational maps[182] from which one can infer the "softness" or "hardness" of the OR molecule and the energies of the transitions from one conformation to another can also be obtained from the calculations. It was found that, despite the abundance of the possible conformations, as a rule only one conformer is present under the conditions of analytical reactions (we shall not consider here tautomeric transformations and the possibility of the simultaneous presence of several tautomeric forms) and its structure is nearly planar (the deviation of the benzene ring from the plane of the naphthalene ring ranges from 0° to 30° depending on the substituents). The possible conformations of the OR are fairly soft. This means that the same functional group, for example, the *o*-arsonazo-*o'*-hydroxy- or *o*-phosphonoazo-*o'*-hydroxy-group, can satisfy the coordination requirements of many metal cations which can in principle interact with it.

This is one of the most important conclusions reached with the aid of conformational analysis. The selectivity of the reagent can be inferred from its softness or hardness. The OR of the arsenazo I and arsenazo III groups are known to be unselective; they interact with many elements, which in fact was to be expected in view of the softness of the conformations of the reagents of this group.

Similar conformational analysis has not so far been carried out for OR of other groups. If it is confirmed that the softness or hardness of the conformations of the OR is directly related to its selectivity, then conformational analysis of compounds of different classes will possess predictive power and will become one of the methods for the theoretical search for specific selective or group reagents. The knowledge of the geometry of the OR and its complexes is essential also for the subsequent quantum–chemical calculation.

5. Estimation of the Reactivities of Organic Reagents

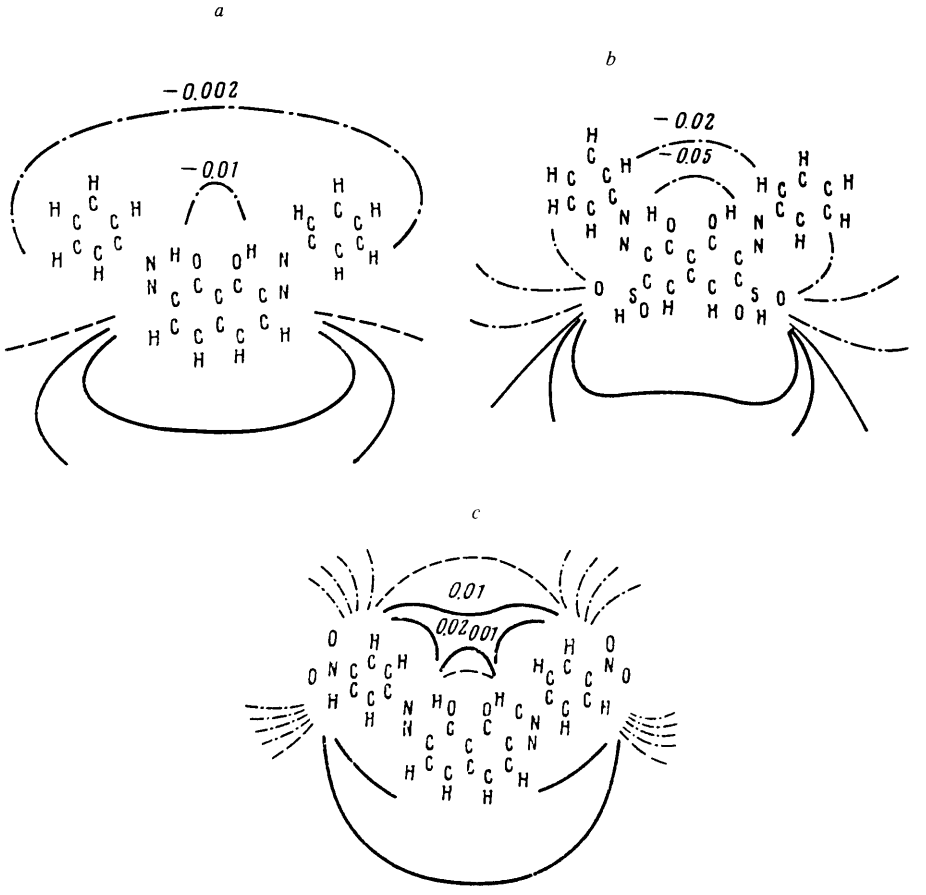
In recent years quantum–chemical methods have been used in the study of the reactivities of OR and of the mechanisms of complex formation reactions. As a rule, the complex formation reaction, especially in its first stage where the metal cation or any other inorganic or organic ion is still comparatively remote from the molecule of the OR, has a distinct electrostatic character. This involves the mutual approach of the charged species and the molecule of the OR, which can be both charged and electrically neutral, but, by virtue of its steric structure and the complex distribution of charges within it, it gives rise to an inhomogeneous electrostatic field along its immediate periphery. The electrostatic field can promote the approach of the metal ion to the reaction centre or conversely can hinder its movement, whereupon the reaction becomes impossible or is retarded. Thus arises the problem of investigating the electrostatic field around the molecule at distances of the order of magnitude equivalent to 2–3 atomic dimensions.

The solution of this problem does not apparently require an especially accurate calculation and the treatment can be restricted to approximations of the type of point charges calculated by the CNDO, INDO, and certain other methods. The methods based on the π-electron approximation are naturally inapplicable in this instance. We shall quote certain model examples demonstrating the dependence of the electrostatic field of the OR molecules on the substituent.

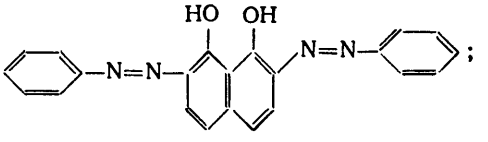
The Figure shows maps of the molecular electrostatic potential calculated for different 2,7-bisazo-substituted 1,8-dihydroxynaphthalenes.[183–185] The distribution of the electrostatic fields in these molecules either facilitates or hinders nucleophilic or electrophilic reactions. In reagents of the group of 2,7-bisazo-substituted chromotropic acid (or 1,8-dihydroxynaphthalene) it is possible to differentiate several functional–analytical groups. We shall consider one of them—the peridihydroxy-group. In the model OR illustrated in Fig.*b* the negative electrostatic potential in the vicinity of the given reaction centre has increased compared with the model reagent in Fig.*a* by a factor of 5 solely as a result of the introduction of two sulpho-groups into the naphthalene nucleus. This model OR is close to a real reagent, namely to a reagent based on chromotropic acid. Naturally the sulpho-groups exert only a weak influence on the distribution of the π-electron density on the atoms incorporated in the conjugation chain of the molecule. This also applies to the

oxygen atoms in the functional–analytical group of the model OR.

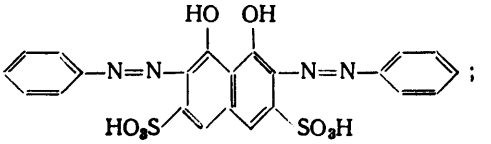
The introduction of nitro-groups in the *p*-positions in the benzene rings of the model OR (Fig.*c*) reverses the sign of the electrostatic potential. The π-electron density on the atoms forming part of the composition of the functional–analytical group hardly changes under these conditions. At the same time the experimental data show unambiguously a sharp alteration of the reactivity of the OR after the introduction of sulpho-, nitro-, amino-, and other groups even



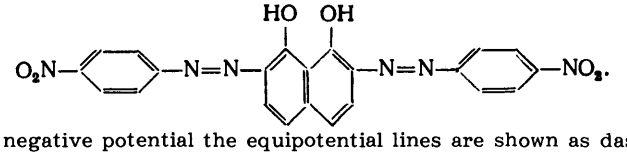
The molecular electrostatic potentials of OR (section in the plane of the molecule): *a*) model reagent of the type of Benzene S without sulpho-groups in the naphthalene nucleus:



b) the Benzene S reagent



c) a model reagent of the type of Benzene S with nitro-groups in the *p*-positions in the benzene rings:



In the region of the negative potential the equipotential lines are shown as dash-dot lines. In the region of the positive potential they are shown as continuous lines; the zero potential lines are indicated by a series of dashes; the numerals denote the potential in e/A^{-1}.

into parts of the molecule remote from the functional–analytical centre. Thus the observed change in the reactivity of the OR can be attributed solely to a change in the molecular electrostatic potential in the immediate (1–3 Å) environment of the functional–analytical centre of the OR.

This comparatively new approach to the theoretical study of the reactivity of the OR can also be used to study their interaction with metal cations to form chelate compounds. The initial structures of the reactants (the structures of the reagents and of the form of the metal under the given conditions) and the structure of the final reaction products have so far been investigated by different procedures; the possible structures of the reaction intermediates have sometimes been discussed. Maps of the molecular electrostatic potentials of the reagents make it possible to follow to some extent the pathway (more precisely the likely site of attack) traversed by the metal ion towards the OR molecule. This may make it possible to specify more precisely the structure of the complex in those cases where there are several sites at which the metal ion can be attached in principle. One cannot rule out the possibility that the selectivity of the OR, the rates of its reactions, and its other analytical characteristics depend to some extent also on the distribution of the molecular electrostatic potential.[185]

In conclusion of the brief survey of the applications of the quantum–chemical methods in the solution of the problems of the theory of the action of OR, we may note that the use of quantum–chemical research techniques has not introduced radical changes into the principal postulates of the theory of the action of OR. On the other hand, during the first decade after the introduction of these methods into the working arsenal of analytical chemistry, it has been convincingly demonstrated with their aid that the theoretical ideas constructed on the basis of traditional research techniques are correct. In the same stage quantum–chemical methods made it possible to obtain much new information about the structure of OR which might have been obtained, albeit with much difficulty, also by means of traditional methods.

The second, modern stage in the application of quantum–chemical methods in analytical chemistry (which began approximately in 1970) is characterised by the possibility of obtaining new information (detailed characteristics of the electronic structures of OR, their electrostatic potential fields, and their reactivities), which cannot be obtained in principle by traditional methods. One can also imagine a transition in the immediate future to a third stage, which will make it possible to predict specific syntheses of OR with specified properties.

6. Kinetics of Colour Reactions

The study of the rates of rapid chemical reactions is important both for the theoretical and practical aspects of analytical chemistry. Certain chemical reactions, which have been regarded for a long time as rapid, are retarded so much under certain conditions that this can introduce significant errors into chemical analysis. It is important to take into account the retardation of the reaction in the development of automatic schemes for the continuous control of industrial processes, for example, in analysis in a stream of liquid. Hitherto few studies have been made on new practical possibilities for increasing sensitivity and selectivity which might be realised if it were possible to employ as analytical forms the reaction intermediates whose principal spectroscopic characteristics can be measured either with the aid of high-speed spectrophotometers or by the application of external influences which arrest or retard the reaction at a specific stage.

However, the mechanisms of the majority of the chemical reactions of analytical importance still remain unelucidated. Even if the composition and structure of the initial reactants and of the analytical product are known, as a rule nothing is known about the structure of the intermediates produced in the interaction of the cation of the given element with an OR having a fairly complex structure.

Until recently, colour reactions were divided into slow and "instantaneous". The kinetics of the latter reactions were hardly investigated, although the rapid reactions might have been in fact of greatest interest for the understanding of the process mechanism because in such cases the mechanism of the formation of complexes operates in a pure form (slow reactions are usually complicated by the hydrolytic process, by the dehydration of metal ions and OR molecules, and other side reactions).

The advances in the study of rapid reactions achieved in related fields of chemistry stimulated the application of the newly developed methods also to the study of analytical colour reactions. Procedures have appeared in recent years for the investigation of the reaction kinetics which make it possible to investigate reactions with a half-reaction time ($t_{1/2}$) ranging from 10^9 to 10 s.[186] It was established in almost all cases that colour reactions are not simple single-stage reactions but proceed with formation of at least one or several intermediates. The study of the reactions of aluminium with Xylenol Orange and Aluminocrezone[187] established that the former reaction proceeds in accordance with a kinetic second-order equation and the latter in accordance with a first-order equation.

In the study of the complex formation reaction between gallium and Methylthymol Blue[188] the formation of the intermediate $Ga(OR)_2$ in the course of the formation of the final complex GaOR was established. It was shown that the process is of first order with respect to both the metal and the OR. Its rate-limiting stage involves the interaction of the complex $Ga(OR)_2$ with the $Ga(H_2O)_n$ cation. The same reagent enters into a first-order reaction with nickel[189] and lanthanium.[190] The slow reaction of arsenazo III with zirconium has also been investigated.[191]

In the case of rapid reactions, the kinetic spectrometric method is very useful in the analysis of a mixture of substances involving complex reactions but differing as regards the formation or decomposition of the complexes. The flow version of the method has been used for the analysis of alkaline earth and certain transition elements.[192] The kinetic method for the quantitative determination of individual lanthanides in the presence of other lanthanides employs the reaction of complexone III (EDTA) with the coloured complexes formed by the lanthanides with Xylenol Orange, it proceeds in accordance with the following scheme:

$$LnX + EDTA \rightleftarrows LnEDTA + X,$$

where Ln is the lanthanide ion, X is the anion of Xylenol Orange, and EDTA represents ethylenediaminetetraacetic acid. In relation to the coloured complex LnX, the above reaction is of first order; in the series of lanthanides the rate of attainment of 50% reaction varies from 236 s^{-1} to 30 s^{-1}.[193] The method developed makes it possible to determine certain lanthanide elements in the presence of a tenfold excess of other lanthanides.

The reaction of UO_2^{2+} with arsenazo III, widely used in analytical chemistry, has also been investigated by spectroscopic-kinetic methods.[144,194] The absorption was measured on a specially designed spectrophotometer with electronic scanning of the spectrum, which ensures the recording of optical absorption spectra in the range 230–800 nm and also the recording of kinetic curves at any wavelength. Analysis of the absorption spectra and of the kinetic curves obtained under different

conditions (concentration, pH of the medium, the presence of other substances in solution, temperature, etc.) permits definite conclusions about the mechanism of the complex formation. It was found that the order of the reaction of UO_2^{2+} with arsenazo III is close to unity; the rate of reaction is proportional to the concentration of one of the components; the determining factor is the concentration of the active, ionised form of the OR. This means that, although the direct interaction of the uranyl ion with the undissociated form of the OR cannot be ruled out, the main process, which determines the rate of reaction, is the interaction of the uranyl ion with the active and especially the dissociated form of the OR.

More complete information about the mechanism of a complex colour reaction can be derived from the study of the absorption spectra of the reaction products recorded by the given apparatus in the course of the reaction. This makes it possible to follow the variation of the concentrations of the individual substances involved in the reaction, i.e. one can obtain their kinetic curves and one can calculate the rate constant for each elementary stage. The constants obtained in this way then have an entirely concrete significance and are not conventional (overall). It is fairly difficult to carry out such an experiment, since it requires, in particular, a high accuracy of the measurements and the ability to resolve unambiguously the complex spectral curves into simple components and also the ability to choose the optimum reaction conditions which will ensure that the reaction proceeds via an unambiguous mechanism. It is likewise essential to have at ones disposal a clear-cut scheme for the interpretation of the results.[184,185]

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Some information about the state and prospects for the development of a branch of science can be obtained by a numerical scientific study of publications. The number of communications devoted to the investigation and general analytical employment of OR varies according to different data from 600 to 1300 per annum, while the annual number of publications on the analytical chemistry of inorganic substances is of the order of 4300–4700.[196,197] The available literature data[198] have shown that different branches of analytical chemistry have undergone one of three types of evolution at different times: regression, saturation, or growth. According to statistical data, studies in the field of OR have not yet reached the stage of saturation and are in the growth stage. The fraction of publications on OR constitutes, according to some data,[197] about 30% of the total number of communications on analytical chemistry.

The main bulk of the applications of OR are in photometry. Photometric analysis is one of the commonest methods. The publications on the photometry constitute ~30–35% of all the publications devoted to analytical chemistry.[199,200] More than half of all the analyses in industry, in agriculture, in medicine, and in the monitoring of the pollution of the environment are performed by spectrophotometric methods. There is reason to believe that in the immediate future (20–30 years) spectrophotometry will become the most important method of chemical analysis. This is indicated by the new ideas and developments in the field of the automation of analysis and analytical apparatus (the flow-injection system and chemical sensors) and also by the advances in the synthesis of new OR.

The synthesis of new highly effective OR is at the present time largely determined by the level of development of the theory of the action of such reagents. This is associated with the fact that the semiempirical search, which has been hitherto the main basis for the creation of new OR, has been virtually exhausted. Theoretical ideas already exist which make it possible to synthesise structural analogues of the known reagents by introducing functional-analytical and other groups or by slight modification of the main carbon skeleton of the molecule of the prototype reagent. This is a reliable way of altering and improving the properties of OR. However, the expected and subsequently observed effects, although satisfactory and sometimes considerable, are not fundamental in the sense that they make it possible to obtain OR specific to some chemical element or to achieve a sharp increase, for example, by an order of magnitude, in the sensitivity of the reaction.

A characteristic feature of the theoretical developments in the last 10–15 years, associated with the application of quantum-chemical and other theoretical research techniques, consists in the search for specific syntheses of new classes and groups of OR with properties specified beforehand. There is reason to believe that this procedure will lead to the creation of new and highly effective OR.

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Advances in the Field of Organoelemental Polymers

V.V.Korshak and N.M.Kozyreva

This review deals with organoelemental polymers containing the elements of various Groups in the Periodic System. The major role of these polymers in many fields of modern technology and national economy is demonstrated. The methods of synthesis of organoelemental polymers used at present and the prospects for the development of this field in the future are considered. It is shown that the heterounit structure of the polymer is a common phenomenon in the chemistry of macromolecular compounds, characteristic also of organoelemental polymers. It has been established that the presence of stable isotopes in polymer macromolecules is one of the causes of the appearance of the heterounit structure.
The bibliography includes 113 references.

CONTENTS

I. Introduction 1091
II. Characteristic features of organoelemental polymers 1092
III. Methods of synthesis of organoelemental polymers 1093
IV. The heterounit structure of organoelemental polymers 1095
V. Stable isotopes as a cause of the heterounit structure of organoelemental polymers 1096
VI. Survey of polymers in terms of Groups in the Periodic System 1097

INTRODUCTION

The chemistry of organoelemental polymers as an independent branch of polymer science has been formulated only in the last forty years. It is characterised by rapid development, which can be accounted for by the possession by organoelemental polymers of valuable qualities such as, for example, high thermal stability, chemical stability, incombustibility and many other specific properties, which make them irreplaceable in practical applications; they have therefore found extensive applications in a number of fields of modern technology.

A.N.Nesmeyanov has pointed out that one of the most important ways of creating new polymers is to employ for their synthesis different elements of Mendeleev's Periodic System.[1] The chemistry of organoelemental compounds is a science of the boundary between inorganic and organic chemistry, which is undoubtedly its positive aspect, since it makes it possible to obtain polymeric compounds combining useful qualities characteristic of compounds of most branches of chemistry.[2] Because of this, many elements of the Periodic System, capable of forming various polymeric compounds, have been the object of chemical research and some of the polymers obtained have already found practical applications in a number of branches of modern technology.[3]

Thus organoelemental macromolecular compounds such as numerous organosilicon polymers, polymers based on various metals and their derivatives, poly(phosphonitrilic chloride) and its various modifications, phosphorylated polystyrene, a series of organoboron compounds, particularly those containing carbaborane groups, and many polymers, and copolymers of fluorinated ethylenes are being manufactured at present on an industrial scale and have found a wide variety of applications.

The concept of organoelemental compounds has been put forward by Nesmeyanov and has been accepted by many investigators.[4]

The history of the chemistry of organoelemental compounds began with the investigations of Andrianov,[5] who obtained in 1937 for the first time organosilicon polymers, and demonstrated their practical value; since that discovery, the field of organoelemental macromolecular compounds has begun to develop.

Undoubtedly one of the most important trends in the future progress of polymer science will be a wide-scale employment of elements of the Periodic System for the synthesis of various polymers;[6] the number of elements used for this purpose increases every year. At the present time 75 elements have already been employed in the synthesis of various macromolecular compounds.[6-8] Among the 106 elements known at present, only the noble gases (6 elements) and the 12 elements belonging to Groups I and VII of the Periodic System, which are univalent and can only play the role of terminating groups, are incapable of producing polymers. Thus, the remaining 88 elements are capable of functioning as chain-forming elements, giving rise to polymeric macromolecules.

Table 1. Elements entering into the composition of the organoelemental polymers synthesised.

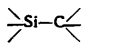
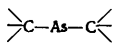
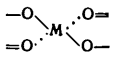
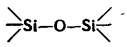
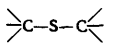
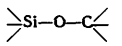
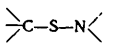
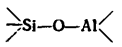
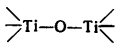
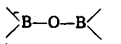
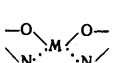
Period	Groups									
	I	II	III	IV	V	VI	VII	VIII		
1	H	—	—	—	—	—	—	—	—	—
2	Li	Be	B	C	N	O	F	—	—	—
3	Na	Mg	Al	Si	P	S	Cl	—	—	—
4	K	Ca	—	Ti	V	Cr	Mn	Fe	Co	Ni
	Cu	Zn	Ca	Ge	As	Se	Br	—	—	—
5	Rb	Sr	Y	Zr	Nb	Mo	—	Ru	Rh	Pd
	Ag	Cd	In	Sn	Sb	Te	I	—	—	—
6	—	Ba	La	Hf	Ta	W	—	Os	Ir	Pt
	Au	Hg	Tl	Pb	Bi	Po	—	—	—	—
7	—	—	—	—	—	—	—	—	—	—

Lanthanides: Ce, Pr, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu.
Actinides: Th and U.

These elements give rise to bifunctional and polyfunctional atoms and groups. The formation of polymeric macromolecules with a homochain structure is fairly common with elements such as boron, carbon, silicon, phosphorus, sulphur, germanium, arsenic, selenium, tin, antimony, tellurium, bismuth, and polonium (in all, 13 elements). Among these elements of the Periodic System, carbon is distinguished by an exceptional ability to form unusually long chains in carbochain polymers, while the remaining elements enumerated above can produce homochain polymers

to a much lesser extent. However, in contrast to this, the number of elements able to participate in the formation of heterochain polymers is very considerable and such compounds include more examples than homochain polymers.

Table 2. The bonds introduced into the composition of organoelemental polymers.

Bond	Bond	Bond
		
		
		
		
		

heating to a temperature exceeding 350 °C, polysiloxanes readily depolymerise, forming cyclic siloxanes. The Si–C bonds then remain unchanged, while the Si–O bonds are ruptured. This difference in behaviour can be explained by the mechanism of the accompanying reaction in which the bonds are rearranged via the formation of an intermediate compound.[13] This reduces the energy barrier to the rupture of the Si–O bond and a cyclic siloxane is formed in accordance with the equation

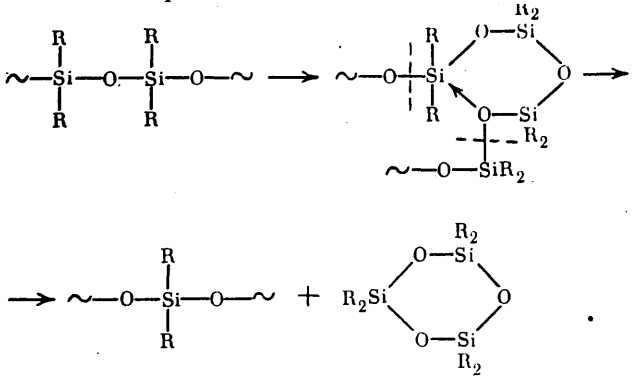
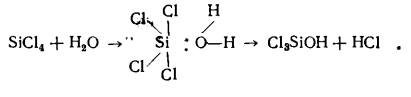


Table 4. The bond energies in heterochain organoelemental polymers.[11,12]

Bond	E_b, kcal mol^{-1}	Bond	E_b, kcal mol^{-1}
B–O	119,3	As–O	64.5
B–N	104,3	Al–C	61.6
B–C	100,0	C–S	61.5
P–O	81,7	Si–S	60.9
C–O	79,0	Si–C	57.6
Si–O	89,3	As–C	54.6
Sb–O	71,0	N–O	37.0
C–N	66,0		

Many other reactions of silicon compounds can be explained in the same way, i.e. by the transition of silicon to a quinquevalent state, as happens, for example, in the hydrolysis of silicon tetrachloride:[15]



However, there are also other ideas concerning the mechanism of these reactions.[16] The bond energies listed in Tables 3 and 4 refer to the homolytic type of bond dissociation reactions. However, bond dissociation reactions of the heterolytic type are encountered among organoelemental compounds much more frequently than those of the homolytic type and it is therefore necessary to take into account the "ionic bond energy", which is characteristic of the reactions which proceed as follows:

$$AB \rightarrow A^- + B^+.$$

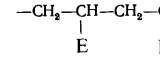
Thus, one can understand why the Si–H bond, for which the homolytic bond dissociation energy is 76.0 kcal mol^{-1}, while the ionic bond dissociation energy is 222.9 kcal mol^{-1}, is more stable in heterolytic reactions than the Si–Cl bond, for which the above energies are respectively 91 and 190 kcal mol^{-1} and the overall energy, amounting to 281 kcal mol^{-1}, is lower than the overall energy in the former case, where it is 298.9 kcal mol^{-1}.[15]

The bonds between the elements in organoelemental polymers are of a different character for different elements. It is possible to arrange the elements in three groups depending on the type of bond characteristic of them,[17] as can be seen in Fig. 1.

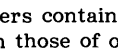
III. METHODS OF SYNTHESIS OF ORGANOELEMENTAL POLYMERS

Organoelemental polymers can be synthesised by means of reactions involving both the polycondensation and polymerisation of the corresponding monomers and via a series of direct modification reactions of various polymers. This results in the formation of polymers of the following three types:

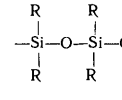
(1) carbochain polymers with an organic main chain of the macromolecule and organoelemental side groups (E):



(2) heterochain polymers containing carbon atoms in the main chain together with those of other elements:



(3) heterochain polymers with an inorganic main chain and organic side groups, such as, for example, polysiloxanes, etc.:



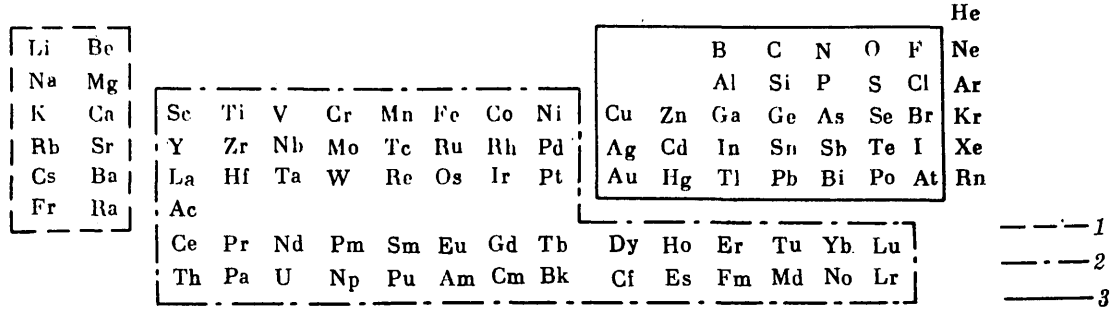


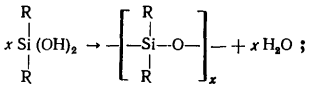
Figure 1. Distribution of the elements in groups as a function of the character of the bond between the atoms: 1) ionic bond type; 2) *d* orbital bond type; 3) covalent bond type.

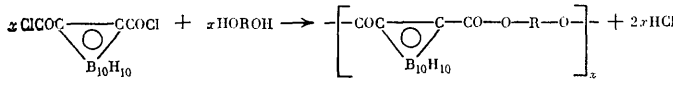
A characteristic feature of organolemeental polymers is the fact that whereas bonds of the $s-p-\sigma$ and $\sigma-\pi$ types are most characteristic of organic compounds, in organoelemental compounds there are also d orbital π-bonds: $d_\pi-p_\pi$ and $p_\pi-p_\pi$, where one or several free electron pairs of the atoms are bound directly to the atom of the element having unoccupied p_π or d_π low-energy orbitals and a suitable symmetry. There are also other types of interaction, which has been demonstrated in relation to numerous new types of compounds belonging to the groups of metallocenes, hydrides, carbaboranes, coordination polymers, etc.

Apart from the elements of the Second Period in the Periodic System, i.e. carbon, nitrogen, and oxygen, bonds of the p_π type are rarely encountered for other elements. Bonds involving $d_\pi-p_\pi$ orbitals are more common in organoelemental compounds, but such bonds are incapable of polymerisation. As a result of this, linear organoelemental polymers are usually synthesised by the polycondensation of bifunctional monomers or by the polymerisation of heterocycles. The advances in the synthesis of organoelemental polymers have been described in a series of reviews and monographs.[4,9-11,14-24]

Several different types of reactions have been used to synthesise organolemental polymers.

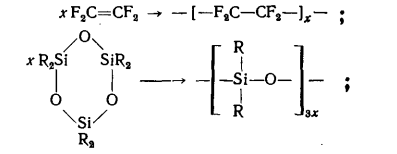
1. Polycondensation of monomers having two and more identical or different functional groups, for example:[25,26]

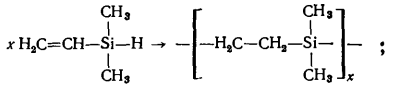


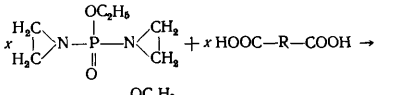


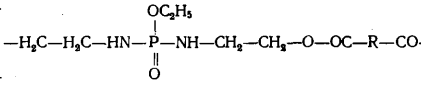
In this case heterochain organoelemental polymers are produced. Two versions of the reaction are then possible, namely "equilibrium" and "non-equilibrium" polycondensations differing in the magnitude of the equilibrium constant,[20,21] which is less than 10^3 for equilibrium polycondensation and more than 10^3 for non-equilibrium polycondensation.

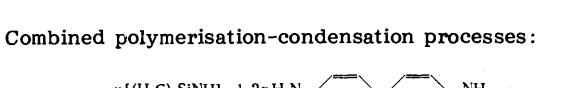
2. Polymerisation of monomers having double bonds or heterocycles and also the migration copolymerisation of the hydrides of silicon and other elements, for example:



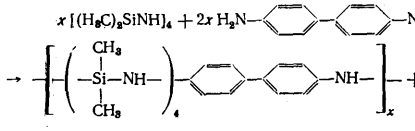








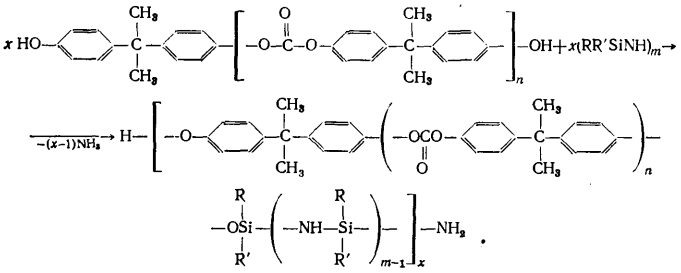
3. Combined polymerisation-condensation processes:



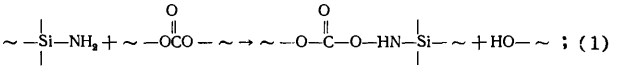
The reaction proceeds not only with the opening of the silazane ring (polymerisation) but also with evolution of ammonia (polycondensation).[27]

The studies[28-35] in which polymers with inorganic and organic molecular chains were obtained by combined polymerisation-condensation processes are of interest. Such polymers can be synthesised from organocyclosilazanes having the general formula $[RR'SiNH]_3$ and diamines or diols. The reaction proceeds both in the presence and absence of catalysts with evolution of ammonia and formation of Si–N bonds in the macromolecular chain. The products exhibit a high thermo-oxidative stability and, depending on the structure of the cyclosilazanes and diols are either solid rubber-like substances with high elasticity or viscous liquids.

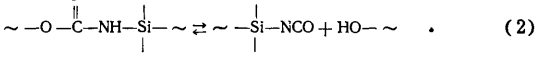
The products of the interaction of organocyclosilazanes with oligocarbonate-diols have been described:[28]



The polymers were obtained by reactions in solvents and in bulk. The reaction in bulk proceeds at a much higher rate but side reactions reduce the molecular weight of the polymer and lead to a less ordered structure of the latter owing to the degradation of the polycarbonate and silazane blocks and the appearance of urethane and isocyanate groups in the macrochain via the following mechanisms:

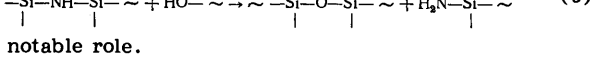


(1)



(2)

At higher temperatures the side reaction

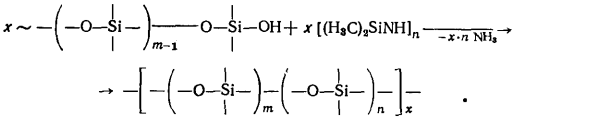


(3)

plays a notable role.

The shift of the equilibrium in reaction (2) to the right, which entails an increase in the concentration of OH groups capable of reacting with the less reactive NH groups in the linear sections of the chain, gives rise to the possibility of condensation reactions leading to the additional evolution of ammonia.

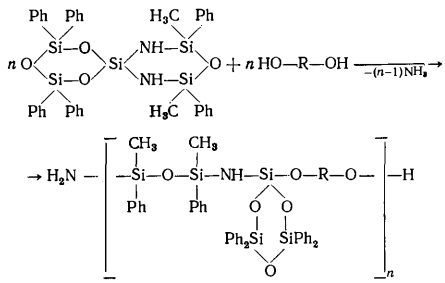
Not only organic diamines and diols but also organosilicon diols can be used in the reactions with diorganocyclosilazanes. Results of practical interest have been obtained by the reaction of $\alpha\omega$-dihydroxypolydimethyl(methylvinyl)siloxanes and dimethylcyclosilazanes:



The rubbers based on such polymers are superior as regards their physicomechanical parameters after thermal ageing to the rubbers based on industrial raw rubber.[29]

Polycarbonate-silazasiloxane block copolymers have been described.[30] They contain not only polycarbonate and silazasiloxane blocks but also urethane groups and have a branched structure.

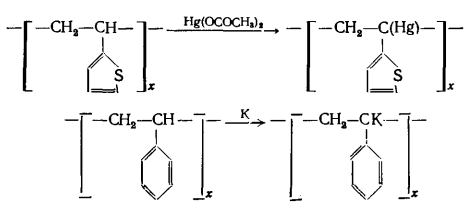
In connection with the different reactivities of the Si–N and Si–O bonds in relation to hydroxy-compounds,[31,32] studies of the polycondensation of organo-spiro-bicyclosilazasiloxanes with organic and organosilicon diols of different structure are of interest. In the ideal case the reaction proceeds via the scheme



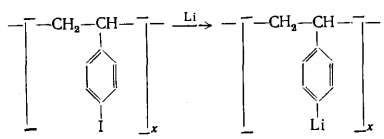
Polymers soluble in organic solvents and cross-linked polymers have been obtained. The block copolymers of organocyclosiloxanes with diols are of great practical interest for the development on their basis of thermostable greases, thermoplastic materials for the storage of information,[33] compositions for coatings,[34,35] etc.

4. The modification of polymers by treatment with metals and their compounds leads to the formation of various organoelemental polymers:

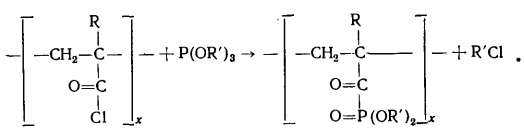
(a) By substituting hydrogen atoms in the polymer chain,[36,37] for example:



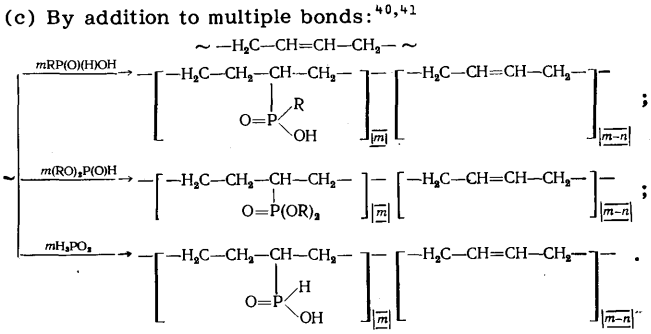
(b) By substituting iodine atoms in poly-p-iodostyrene:[38]



or by substituting chlorine atoms in the polymer:[39]

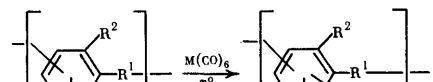


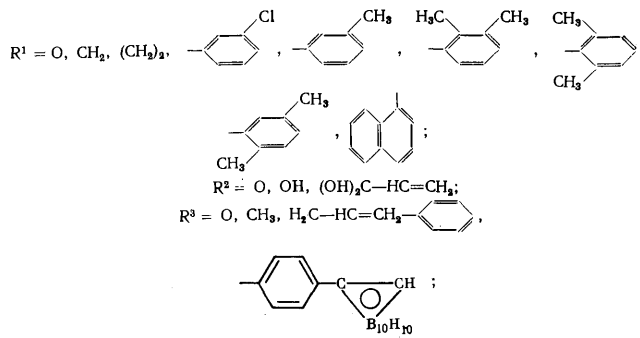
(c) By addition to multiple bonds:[40,41]



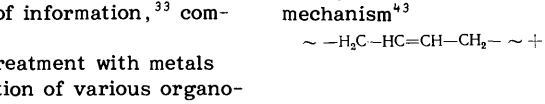
(d) By the π-complex formation reaction involving polymers.

π-Arenemetal tricarbonyl polymeric or oligomeric complexes have been obtained via the following mechanism:[42]





Polymeric π-complexes of metals are obtained via the mechanism[43]



The reactions of the chlorides of *o*-, *m*-, and *p*-carbaboranedicarboxylic acids with cellulose lead to the formation of the corresponding cellulose esters which are able to produce a residue on heating with a high "coke content".[44]

There exist also a wide variety of other modification reactions leading to the formation of organoelemental polymers. They all result in the formation of heterounit polymers.

IV. THE HETEROUNIT STRUCTURE OF ORGANOELEMENTAL POLYMERS

The concept of the heterounit structure of polymers is equally applicable to organoelemental polymers, as it is in fact to all other macromolecular compounds, being a general phenomenon in this field of chemistry.[45,46] The syntheses of polymers involve various side reactions leading to the formation of anomalous units and hence to the appearance of heterounit polymers. Various reactions and other causes responsible for the formation of anomalous units in the polymerisation and polycondensation of monomers and also in the modification of polymers are presented below. The statistical distribution of isotope atoms, which occurs in all polymers, should be added to this factor. As a result, a more correct formula for real polymers is as follows:

$$-[-(M)_{|m|}-(A)_{|n|}-]_x-\ ,$$

where M is the normal unit, A the anomalous unit and *m* and *n* are coefficients indicating the statistical distribution of anomalous units of different kinds. On the other hand, the formula usually employed, i.e.

$$-[-M-]_x-$$

is idealised and is never really valid.

The formation of heterounit polymers as a result of various side reactions proceeds differently depending on the character of the latter. This is clearly seen when the

characteristics of the polycondensation, polymerisation, and modification reactions are compared (Figs.2, 3, and 4). Each of these reactions involves numerous chemical transformations of different kinds which results in many different anomalous units and heterounit structures of different types. Fig.2 presents the set of polycondensation reactions, including numerous reactions leading to a heterounit structure.[45] Fig.3 presents the set of all the possible polymerisation reactions, including normal reactions and those resulting in a heterounit structure.[45] Finally, Fig.4 presents the set of modification reactions, including those resulting in a heterounit structure,[45] which happens mainly in incomplete substitution processes.

Set of polycondensation reactions	Normal polycondensation reactions	Onset of chain growth
		Chain growth
		Arrest of chain growth
	Polycondensation reactions and other causes of the formation of heterounit polymers	Branching of macromolecules
		Partial isomerisation of units
		Joint polycondensation
		Incomplete cyclisation in polyheteroarylenes
		Irregular structure formation in macromolecules
		Different combinations of asymmetric units
		Conformationally-specific polycondensation
		Steric disorder of units
		Dehydrogenation, dehydration, and dehydrochlorination of monomers and polymers
		Isomerisation of monomer
		Addition to the double bonds of unsaturated monomers and polymers
		Competing polycondensation reactions of various functional groups of polyfunctional monomers
		Non-uniformity in the involvement of the monomers in the reaction
		Programmed polycondensation
		Disturbance of natural programmed polycondensation processes (information errors)
		Statistical distribution of atoms of stable isotopes in polymer macromolecules
		Other side reactions

Figure 2. The set of polycondensation reactions.

An important feature of organoelemental polymers, which is frequently encountered in practice, is the possibility of the formation of both linear and branched or three-dimensional polymers. This difference is determined by the functionality of the initial monomer or oligomer.[50] It is therefore necessary to distinguish the following types of functionality, namely the possible functionality Φ_p, the practical functionality Φ_{pr}, and the relative functionality Φ_r. When the possible functionality $\Phi_p = 2$, a linear polymer is produced whereas in the case where the values of the possible functionality are greater than 2 the product is a branched or a three-dimensional polymer.[51]

Set of polymerisation reactions	Normal polymerisation reactions	Onset of chain growth
		Chain growth
		Chain termination
	Polymerisation reactions and other causes of the formation of heterounit polymers	Branching of macromolecules
		Partial isomerisation of units
		Joint polymerisation
		Different combinations of units
		Stereospecific polymerisation
		Recombination of macroradicals
		Disproportionation of macroradicals
		Partial dehydrogenation of polymers
		Partial dehydrochlorination of polymers
		Partial dehydration of polymers
		Irregular structure formation in macromolecules
		Steric disorder of units
		Statistical distribution of atoms of stable isotopes in polymer macromolecules
		Other side reactions

Figure 3. The set of polymerisation reactions.

V. STABLE ISOTOPES AS A CAUSE OF THE HETEROUNIT STRUCTURE OF ORGANOELEMENTAL POLYMERS

Among the causes giving rise to a heterounit structure of polymers, mention should be made of the presence of stable isotopes of polymer-forming elements, which are distributed statistically in the macromolecular chain. The influence of isotopes has been demonstrated particularly strikingly in relation to the copolymers of ethylene, propene, and styrene by comparing them with their deuteriated analogues.[46-48] The copolymers have the following structures:

$$-\left[-(-CH_2-CH_2-)_{\overline{m}}-(-CD_2-CD_2-)_{\overline{n}}-\right]_x-$$

$$-\left[-\left(-CH_2-\underset{CH_3}{CH}-\right)_{\overline{m}}-\left(-CD_2-\underset{CD_3}{CD}-\right)_{\overline{n}}-\right]_x-$$

$$-\left[-\left(-CH_2-\underset{C_6H_5}{CH}-\right)_{\overline{m}}-\left(-CD_2-\underset{C_6D_5}{CD}-\right)_{\overline{n}}-\right]_x-.$$

In all the cases investigated, a distinctive effect of the content of hydrogen isotopes on the properties of the polymers was observed.

Table 5 lists the stable isotopes of the elements used to synthesise polymeric structures.

Table 5. The stable isotopes of polymer forming elements.[49]

Element	Stable isotopes	Relative distribution, %
Hydrogen	H, D	H (99.984), D (0.016)
Boron	^{10}B, ^{11}B	^{10}B (18.8), ^{11}B (81.2)
Carbon	^{12}C, ^{13}C	^{12}C (98.9), ^{13}C (1.1)
Nitrogen	^{14}N, ^{15}N	^{14}N (99.6), ^{15}N (0.4)
Oxygen	^{16}O, ^{17}O, ^{18}O	^{16}O (99.76), ^{17}O (0.04), ^{18}O (0.20)
Silicon	^{28}Si, ^{29}Si, ^{30}Si	^{28}Si (92.6), ^{29}Si (4.3), ^{30}Si (3.1)
Chlorine	^{35}Cl, ^{37}Cl	^{35}Cl (75.4), ^{37}Cl (24.6)

Set of modification reactions	Normal modification reactions	Substitution of a hydrogen atom, a halogen atom, and a hydroxy-group
		Structure formation in polymers
		Exchange reactions of heterochain polymers
		Degradation of macromolecules
		Elimination of water, hydrogen halide, etc.
		Isomerisation of macromolecules
	Modification reactions and other causes of the formation of heterounit polymers	Incomplete substitution of a hydroxy-group, a hydrogen atom, a halogen atom, etc. in the polymer macromolecule
		Grafting to macromolecules
		Partial oxidation of macromolecules
		Irregular structure formation in macromolecules
		Partial degradation of macromolecules
		Incomplete exchange in heterochain polymers
		Partial structure formation in polymer
		Partial addition to multiple bonds
		Partial elimination of water, hydrogen halide, etc.
		Incomplete isomerisation of macromolecules
		Statistical distribution of atoms of stable isotopes in polymer macromolecules
		Other side reactions

Figure 4. The set of modification reactions.

VI. SURVEY OF POLYMERS IN TERMS OF GROUPS IN THE PERIODIC SYSTEM

The organoelemental polymers known at the present time are divided into two large groups depending on the structure of the main chain—homochain and heterochain polymers.[9,11] Among homochain polymers, the group with the largest number of representatives is that of carbochain polymers. Homochain polymers based on other elements are extremely few in number and are not quite so important. However, we may mention that homochain polymers of the following eight elements are known at the present time: C, B, Si, Ge, P, S, Sb, and Se.

Heterochain polymers based on a large number of elements in the periodic system are a much more important class of organoelemental polymers. Almost all the elements are capable of forming heterochain polymers. Various polymers of the elements in the Periodic System, starting from Group I and extending to Group VIII, are now known. Heterochain polymers containing the following Group I elements have been described: H, D, Li, Na, K, Cu, and Ag. Among them, the copper and hydrogen compounds are of practical importance. Polymers containing isotopes of various elements are of considerable interest for the understanding of the characteristic features of the reactions and properties of polymers.[46-49] Thus polymers containing a heavy hydrogen isotope (deuterium) are important for the explanation of the heterounit structures of a series of polymers. "Heavy" polymers in which the hydrogen has been fully or partly substituted by deuterium have been obtained with the aid of this procedure. The properties of such "heavy" polymers differ significantly from those of their hydrogen analogues.[46-49] "Heavy polyethylene", "heavy polypropylene", and "heavy polystyrene" have been obtained in this way:[46-49]

$$-\left[-CD_2-CD_2-\right]_x- \quad -\left[-CD_2-\underset{CD_3}{CD}-\right]_x- \quad -\left[-CD_2-\underset{C_nD_5}{CD}-\right]_x- .$$

Heterochain organoelemental polymers containing the following Group II elements are known: Be, Mg, Zn, Ca, Ba, Cd, and Hg. Homopolymers and copolymers of metal-containing alkali and alkaline earth metal (Ca, Sr, and Ba) monomers have been described.[52-54] Magnesium compounds have found particularly extensive applications in organic synthesis.

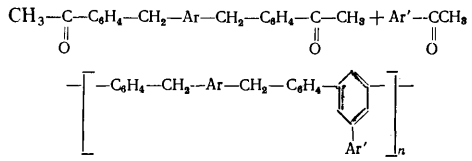
Polymers containing B, Al, Ga, Ce, and Tl are known for Group III elements. Polymers containing boron and aluminium have attracted particular attention among them. The formation of coordination polymers as well as a wide variety of condensation reactions leading to the formation of macromolecular compounds are characteristic of Group III elements.

The homochain polymers of boron, whose main chian consists only of B–B bonds, constitute a group of polymers with a small number of representatives, which can apparently be accounted for by their tendency to oxidise and hydrolyse.[55,56] Depending on the molecular weight, the polymers are colourless or yellow or brown powders. Some polymers are soluble in organic solvents, but no solvents have been found for the majority of them. The thermal stability of the polymers with B–B bonds does not exceed 200 °C. Heterochain boron compounds with B–C bonds have not found practical application because of the considerable tendency of the B–C bond to hydrolyse and, in aliphatic compounds, to oxidise.

Polymers containing polyhedral borane groups have appeared only in the last 15–20 years. The information available in the patent literature indicates their possible use as protective coatings on glass, wood, metals, and other surfaces.[57] In compositions with other polymers, they can be used as thermostable rubbers[57] or as highly effective rocket fuel.[58]

The discovery of carbaborane was the first step towards the creation of a new field of the chemistry of organoboron polymers containing carbaborane fragments. Carbaborane-containing polymers are obtained by both polymerisation and polycondensation methods. However, the polycondensation method of synthesis has come to be most widely used. Among the carbaborane-containing polymers of the polycondensation type, polyphenylenes,[59-63] phenol-formaldehyde polymers,[64-67] polyesters, polyamides,[68-76] and polysiloxanes[77-87] have been most thoroughly investigated at the present time.

Polyphenylenes, the first stage in the synthesis of which can be represented schematically in the following manner have been described:[59,60]



where Ar = *o*-, *m*-, or *p*-carbaboranylene and Ar' = phenyl, benzyl, or *o*-, *m*-, and *p*-carbaboranyl.

It has been noted[59,60] that the polycondensation reactions of the above compounds proceed unambiguously and are accompanied by the formation of dyphone and also linear and cyclic polyvinylene fragments. The oligophenylenes synthesised contain *o*-, *m*-, or *p*-carbaborane groups in the main macromolecular chain and in some cases also in the side chain and are highly soluble in many organic solvents. All the carbaborane-containing oligophenylenes have low molecular weights (MW = 1100–4600) and their softening temperatures are in the range 150–220 °C; at 400–500 °C in an inert atmosphere in the course of 4 h or in a pressing process involving heating to 400–450 °C (and a pressure of 1000 kg cm^{-2}), they are converted into infusible and insoluble three-dimensional polymers as a result of their interaction via terminal acetyl and ketyl groups. Polyphenylenes with *o*-, *m*-, and *p*-carbaborane fragments in the main chain exhibit an enhanced adhesion to glass fibre, which amounts to 250–350 kg cm^{-2}, and have been recommended as thermostable binders for glass plastics.[60]

Oligophenylenes containing carbaborane fragments in the side chain have been obtained.[59,62] The authors noted that the introduction of carbaborane fragments into the side chain of polyphenylene increases the thermal stability of the latter, but this effect is smaller than for the polyphenylenes containing carbaborane groups in the main macromolecular chain.

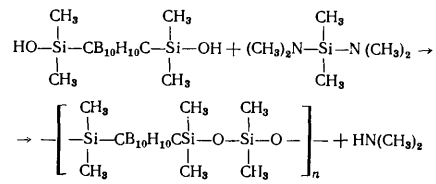
In order to simplify the synthesis of polyphenylene with *o*-carbaborane frgaments, the more readily available ethyl ketal or acetylbiphenylyl-*o*-carbaborane has been used instead of 4-acetylbenzyl-*o*-carbaborane, the synthesis of which is technologically complex.[61,63] The oligophenylenes obtained were less soluble in organic solvents but their thermal stability proved to be greater.

Studies on the synthesis and properties of carbaborane-containing phenol-formaldehyde oligomers of the resol type have continued in recent years.[64,65] The chemical reactions occurring in resols and resites based on 1,2-bis(4-hydroxyphenyl)-*o*-carbaborane on heating under various conditions have been studied. It has been established that in the temperature range 50–200 °C the formation of resol structures proceeds via the usual mechanism not involving the *o*-carbaborane groups. Above 200 °C, significant chemical transformations of the *o*-carbaborane fragments of resites take place and the degree of conversion depends on the heating conditions (in air or *in vacuo*). The high-coke residue from *o*-carbaborane-containing resites its due to the oxidation of the B–H bond in the *o*-carbaborane nuclei, which has been confirmed by X-ray diffraction and EPR data.[64–66] Adhesives with a high strength and thermal stability have been obtained from *o*-carbaborane-containing resol oligomers.[67]

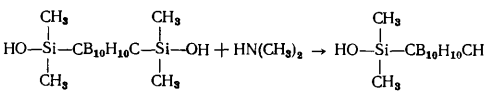
There has been an increase of interest recently in the study of the properties of the polyesters and polyamides with carbaborane fragments obtained previously.[68–76] The structural-chemical transformations of *o*- and *m*-carbaborane-containing polyarylates on isothermal heating in the temperature range 225–235 °C have been investigated by infrared spectroscopy. It has been established that processes involving the rupture of the ester linkage, changes in the carbaborane fragments (a change in the B–H bond and the appearance of the B–O–B bond), and the formation of cross-linked structures take place at a temperature as low at 225 °C. A comparative study of the thermal stabilities of polyarylates with various structures has been carried out.[70] Problems concerning the chemical stability of polyamides with carbaborane-containing fragments and their anti-friction properties have been examined.[71–76]

The most numerous and best investigated class of carbaborane-containing polymers is that of carbaboranesiloxane polymers. Investigations of the synthesis of *m*-carbaborane-containing polysiloxanes of the "Dexsil" type and of their properties are being continued vigorously. The difficulty of the synthesis and vulcanisation of these polymers, in which a high thermal stability is combined with elasticity, prevents their practical application.

A new method of synthesis of linear "Dexsils" is based on the condensation of an *m*-carbaborane-containing disilanol with a reactive silane, for example, bis(*NN'*-dimethylamino)-dimethylsilane or bis(*NN'*-dimethylcarbamato)dimethylsilane, under mild conditions:

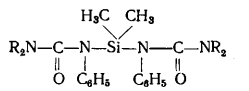


The side reaction

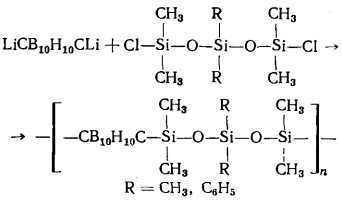


prevents the formation of "Dexsils" with higher molecular weights.

"Dexsils" with molecular weights in excess of 25000 have been synthesised using stable bis(ureido)silanes as reactive silanes:[77,78]



Another, very convenient method of synthesis of "Dexsils" directly from *m*-carbaborane via the following mechanism has been proposed:[79]



However, the molecular weights of the polymers thus obtained are low.

Studies have been made of the thermal, thermo-oxidative, and hydrolytic stabilities of poly-*m*-carbaboranylene-siloxanes.[80,81] The practical value of poly-*m*-carbaboranylenesiloxanes, in which a high thermal stability (up to 500 °C) is combined with excellent fire resistance (oxygen index 62), has been noted in Peters' review.[82] These polymers have found extensive applications as liquid phases in gas chromatography for the separation of organosilicon and

organic substances[83] and for the analysis of polycyclic aromatic hydrocarbons.[84]

Adhesive compositions, capable of being used for a long time at 600 °C and of withstanding a temperature of 1200 °C for brief periods, have been produced on the basis of *m*-carbaborane-containing polysiloxanes.[85] Poly-*m*-carbaboranylenesiloxanes are used for the coating of conductors and other articles which have to withstand a temperature of ~300 °C[82,86] and also as lubricating materials for high-temperature nuclear equipment.[87]

Thus the literature data published in recent years permit the conclusion that boron-containing polymers and particularly carbaborane-containing polymers have attracted the attention of investigators. The study of the properties of these polymers and their modifications and the search for new simpler ways of synthesising them are of particular interest.

Polymers containing the following Group IV elements have now been synthesised: C, Si, Ti, Ge, Zr, Sn, and Pb. This group of polymers has the greatest number of representatives: polymers containing carbon and silicon are of particular importance in practice.

The continued interest in the creation of new materials with a set of valuable properties, some of which are characteristic of organosilicon polymers (frost resistance, thermal stability, permeability, etc.) has stimulated further development of studies on the synthesis and properties of polyorganosiloxanes and copolymers based on them.[88]

The polydiethylsiloxane rubber, which has been studied in detail recently,[89,90] has extremely interesting properties. The properties of various block copolymers containing fragments of the polydiethylsiloxane chain as a flexible block have attracted attention. Polycarbonate-siloxanes, polycarbonate-urethane-siloxanes, polysulphone-siloxanes, and polyarylate-siloxanes have been most thoroughly investigated and have been adequately described.[91,92]

Polyorganosiloxanes containing metal atoms in the polymer chain have found extremely varied practical applications.[93] Polyaluminoorgano-siloxanes are used as catalysts of the hardening of various organosilicon oligomers.[93] Polystannoorganosiloxanes are employed as hydraulic liquids, thermostable coatings, inhibitors of the oxidation of siloxane liquids, and modifying agents for rubber mixtures based on siloxane raw rubbers.[93] Polytitano-organosiloxanes, polyvanadium-phenylsiloxanes, and polyzirconium-aluminophenylsiloxanes are effective catalysts of various processes.[93] A technology for the industrial manufacture of many polymers has been developed.[94]

Among polymers containing Group V elements, extremely numerous and practically important products with elements such as N, P, As, Sb, and Bi are encountered. Among them the nitrogen and phosphorus compounds are especially important. The introduction of a phosphorus atom into the macromolecules of various polymers makes it possible not only to imporve their important properties such as thermal stability and colour fastness,[95] fire resistance,[96] hydrophilicity,[97] and physicomechanical indices but also to synthesise polymeric materials capable of ion exchange as well as polymers possessing oxidation-reduction properties and biological activity.[98]

Phosphorus-containing polymers can be synthesised by polymerisation, polycondensation, and chemical modification methods. The copolymerisation of unsaturated organic monomers with an organophosphorus monomer is one of the promising ways of obtaining organophosphorus polymers, which permits an extensive modification of the properties of various polymeric materials.

Organophosphorus monomers enter into the free-radical copolymerisation reaction with virtually all the usual vinyl monomers and the introduction of small amounts of phosphorus frequently imparts new and valuable qualities to the polymers. The diene, methacrylate, and styrene derivatives of phosphorus are of greatest interest for copolymerisation.[99]

Depending on the chemical nature of the fragments incorporated in the copolymer chain, the copolymers of phosphonodienes are plastics or rubber-like materials and, by virtue of the presence of polar phosphoryl groups, they exhibit an improved adhesion to glass, metals, and other surfaces. When phosphonodienes are introduced into a copolymer, the most significant effect is manifested in the improvement of the fire resistance of the material. Methods for the preparation of transparent colourless, incombustible organic glasses have been developed on the basis of copolymers of methyl methacrylate and phosphono-2,3-dienes.[99]

The introduction of phosphorus-containing groups into the polymer chain leads to the self-stabilisation of polymers.[100] The introduction of such groups via the copolymerisation of the monomers has not so far become of great practical importance. However, this procedure has significant advantages in special methods for the processing of polymers, in particular for the formation of poly(vinyl chloride) materials from solution.[101]

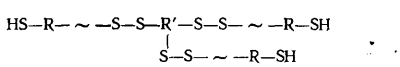
The most important feature in the chemical modification of polymers involves the introduction of phosphorus-containing groups via polymer-analogue reactions.[41,102] Phosphorylation of synthetic rubbers increases their thermal stability and lowers their combustibility.[100] Phosphorylation of chlorosulphonated polyethylene greatly improves its technological properties and strength parameters.[100] The study of the phosphorylation reactions of chloromethylated polystyrene and the copolymers of styrene with aromatic vinyl compounds has shown that the polymers obtained possess ion-exchange properties, effective mechanical properties, and improved porosity and thermal stability.[100] The phosphorylation of polymers at the stage in which degradation processes develop gives rise to a secondary stabilisation of the polymeric products and improves their operating characteristics.[100]

There has been an apprecialbe growth of interest in the last decade in polyphosphazenes—polymers with inorganic main molecular chains consisting of alternating phosphorus and nitrogen atoms in organic or organoelemental frameworks surrounding the phosphorus atom. The interest in these polymers is due to their high thermal stability and fire resistance,[104] their effective elastic properties,[105] and their improved resistance to degradation by oxidants and reductants.[95]

The use of polyphosphazenes for medical purposes, which has been developing in two directions, is of great interest. The first application involves the study of their biological compatibility and thrombogenic properties in order to elucidate the possibility of using such polymers in surgery. Thus the high stability of polyfluoroalkoxyphosphazene as regards clotting, compared with ftoroplast-4 [a type of PTFE] and polyethylene for medical purposes has been demonstrated.[106] In combination with the constancy of its physicomechanical and mechanical properties after prolonged contact with a medium close in composition to that of blood, this renders this polymer extremely promising for the manufacture of articles used in vascular surgery. The other type of research on polyorganophosphazenes for medical purposes involves the synthesis of polyphosphazenes as carriers of medicinal drug molecules and as absorbable surgical materials.[107]

For Group VI elements, polymers containing O, S, Cr, Se, Mo, W, and U are known; the most important of these are oxygen- and sulphur-containing polymers. The great interest of investigators in sulphur-containing polymers and their increasing practical use are associated with their valuable properties and the ready availability of the raw materials combined with the simple methods of their synthesis.

Interesting representatives of sulphur-containing polymers are polysulphide oligomers containing sulphur in the main chain. The majority of industrial polysulphide oligomers have a weakly branched structure with terminal SH groups:



The presence of such end groups, which are readily oxidised under mild conditions makes it possible to employ these oligomers as a basis for the preparation of composite materials (materials for hermetic seals, mastics, and casting compositions).[108]

The different operating conditions for hermetic materials of different brands are striking. Thus the minimum operating temperature varies from −30° to −60 °C, while the maximum operating temperature varies from +80° to +140 °C. The difference between the minimum operating temperatures of hermetic materials can be accounted for by the recipe specifying their composition. The maximum operating temperature usually depends on the presence, type, and amount of the modifying additive, the type of vulcanising agent, and the filler. Polysulphide oligomers are non-toxic, burn with difficulty, and are non-explosive. Hermetic materials based on them do not have a harmful effect on man.[109]

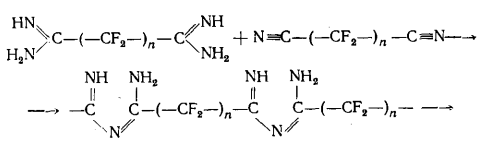
Among the polymers containing Group VII elements, compounds with F, Cl, Br, I, and Mn are known, those containing fluorine and chlorine being most widely used. Many fluorinated plastics play an important role in the development of modern technology.

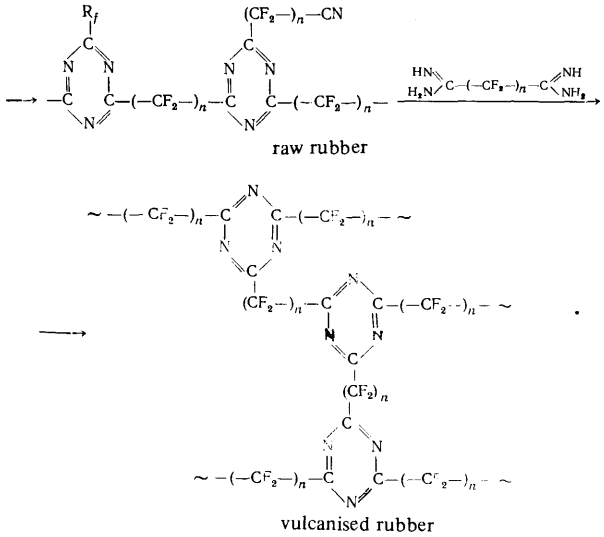
Carbochain fluorine-containing polymers are most widely used at the present time. Among them, polytetrafluoroethylene (PTFE) is the most thermostable polymer. It is resistant to the action of oxygen up to comparatively high temperatures, but it is a high-melting crystalline material and becomes ealstic only at temperatures close to the decomposition temperature. Despite its unique properties, the making of articles from PTFE is fairly difficult. Methods based on sintering an mechanical treatment are largely employed.

In order to obtain elastomers from fluorinated hydrocarbons, it is necessary to disturb the regularity of the structure of the polymer chain in order to rule out or diminish crystallisation. For this purpose, various "hinged" groups are introduced by copolymerising PTFE with fluorinated or non-fluorinated monomers. Tetrafluoroethylene copolymerises effectively with both fluorinated and non-fluorinated monomers, forming numerous copolymers with a wide range of valuable properties. In recent years it has been possible to create a series of tetrafluorethylene copolymers which, whilst retaining many of the valuable properties of PTFE, can be worked with the aid of the usual equipment.[110]

The introduction of the triazine ring into chains of perfluorinated polymers makes it possible to increase the thermal stability of the raw rubber and gives rise to the possibility of obtaining rubbers whose vulcanisation network has a thermal stability not inferior to that of the main chain. Methods are known for the introduction into some of the triazine rings of perfluorinated groups with functional substituents, which can be employed for vulcanisation.[110]

The starting material for the preparation of perfluoroalkylenetriazine rubbers consists of the dinitriles of perfluorinated dicarboxylic acids:





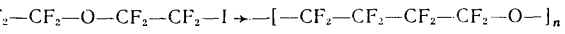
raw rubber

vulcanised rubber

According to literature data the rubbers produced from triazine raw rubbers retain a fairly tensile strength after heating for a long time. Perfluoroalkylenetriazine raw rubbers are resistant to the action of strong acids, but are decomposed by bases, including ammonia.

Apart from the triazine ring, other heterocyclic systems can be introduced into the polymer chain; oxadiazoles, benzimidazoles, thiadiazoles, pyromellitimides, etc.

Perfluorinated rubber-like polymers based on olefin oxides can be synthesised from diiodo-derivatives in the presence of mercury on irradiation with ultraviolet light. The resulting elastomer has excellent low-temperature properties and a high thermal stability:[110]



Despite the interesting properties of this elastomer, it is only a model compound, because of the difficulty of obtaining the initial diiodo-derivatives. A method of synthesis suitable for practical application has not yet been found.

Fluorinated olefins are usually copolymerised with tetrafluoroethylene or vinylidene fluoride in an aqueous emulsion and it is also possible to carry out the process in a solvent.

At temperatures up to 200–250 °C, the structure of the raw fluororubbers does not undergo appreciable changes for a long time. In terms of their resistance to organic liquids, particularly at high temperatures, the rubbers prepared from the raw fluoro-rubbers are appreciably superior to the rubbers obtained from all other sources. In view of the extremely wide range of applications of raw fluoro-rubbers (materials for hermetic seals), their most important parameter is the residual compressive deformation. Because of this, investigators have concentrated their efforts on improving this characteristic.

Group VIII elements of the Periodic System which have entered into the compositions of polymers synthesised are iron, cobalt, and nickel. The three elements form part of various thermostable coordination polymers whose properties are determined by the chemical nature of the ligand and the metal forming the coordination centre.

The infusibility and insolubility of the majority of the coordination polymers restrict their wide-sclae application. Studies designed to obtain metal complex iron, cobalt, and nickel polymers without their conversion into a three-dimensional structure, which ensures the retention of solubility by the polymers, are therefore of great interest.[111,112] The polymeric complexes synthesised contain metal carbonyl

fragments in the polymer chain, are soluble in organic solvents, and are capable of forming strong films and coatings with a high degree of adhesion to glass and metals. After the films have been subjected to a heat treatment, they undergo structure formation and an increase in strength and the polymer acquires at the same time new properties. Thus the decomposition of the iron tricarbonyl complex in the polymer matrix involves the formation of a metallic phase and the film acquires ferromagnetic properties.[113]

Metal-containing polymers have found applications in a wide variety of fields: an application associated with the improvement of various properties of polymers and compositions based on them and an application based on the appearance of new properties due to the presence of the metal in the main chain or a side chain.[21]

It is thus clear that the development of the fields of organoelemental polymers has now placed at the disposal of polymer science a considerable number of organoelemental polymers, many new examples of which are being added each year.

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In conclusion of the discussion of the advances in the synthesis and investigation of organoelemental polymers, we may conclude that a new major field of polymer science has now arisen and is developing vigorously.

At the present time this field embraces a large number of organoelemental polymers, for the synthesis of which 75 elements of Mendeleev's Periodic System have been used and the number of polymers of this type increases rapidly. Organoelemental polymers are substances with a wide range of specific properties which depend both on their composition and on their chemical structure.

As a result of the wide-scale application of the elements of the Periodic System in the synthesis of polymers, not only a quantitative growth and the appearance of many new qualitative changes in the structure of the groups forming the polymer macromolecules but also the appearance of a new set of properties have been observed.

The considerable advances in the synthesis and study of groups of organoelemental polymers such as polysiloxanes, polymetallosiloxanes, phosphorus-containing polymers (including polyphosphazenes), organoboron (including various polycarbaboranes), organosulphur, and coordination polymers of the chelate type (including polyferrocenes), as well as polymers incorporating various fluorocarbons and their copolymers must be specially emphasised.

Organoelemental polymers include a large group of thermostable polymers, a series of substances with valuable biological properties, and also substances with a high electrical conductivity and semiconducting properties, a high elasticity, and an oustanding strength and hardness.

The main task of the investigators concerned with polymers is the expansion of the range of organoelemental macromolecular compounds, the development of new and improvement of existing methods of synthesis of such substances, and the study of their properties with the aim of their practical application.

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Kinetics and Mechanism of the Catalytic Cyclotrimerisation and Polycyclotrimerisation of Isocyanates

A.K.Zhitinkina, N.A.Shibanova, and O.G.Tarakanov

The available literature data concerning the kinetics and mechanism of the cyclotrimerisation and polycyclotrimerisation of isocyanates in the presence of catalysts of various kinds are presented and analysed in this review. Attention has been concentrated on studies published during the last ten years. A number of features characterising the kinetics of the cyclotrimerisation of isocyanates have been deduced from the information about the process presented here. The mechanism of the reaction in the presence of basic catalysts is examined.
The bibliography includes 263 references.

CONTENTS

I. Introduction 1104
II. Catalysis by tertiary amines and catalytic systems based on them 1104
III. Catalysis by tin, zinc, antimony, phosphorus, and arsenic compounds and metal naphthenates and acetylacetonates 1109
IV. Catalysis by alkali metal and quaternary ammonium carboxylates 1112
V. Some features of the kinetics of the cyclotrimerisation of isocyanates and the proposed process mechanisms 1115

I. INTRODUCTION

Among the numerous reactions of isocyanates, their cyclotrimerisation (CT) and polycyclotrimerisation reactions have found extensive applications at the present time. This can be accounted for by a number of factors, namely the high thermal stability, fire resistance, and resistance to the action of organic solvents of corrosive media of isocyanurate-containing polymeric materials and the large assortment and availability of catalysts of the cyclotrimerisation of isocyanates, which permit the specific synthesis of the polymers under mild conditions.

The CT reaction of isocyanate groups is used in polymerisation processes in the preparation of coatings, films, varnishes, elastomers, adhesives, and various resins.[1-9] However, the greatest number of advances in this field concern the preparation of polyisocyanurate-containing foam plastics,[10-50] which have been finding increasing applications as thermostable, fire resistant, thermally insulating, electrically insulating, sound proofing, and constructional materials in applied fields such as building, refrigeration technology, instrument making, transport, shipbuilding aeroindustry, space technology, etc.[29,30,51-53]

Despite the fact that the cyclotrimerisation of isocyanates was achieved more than a century ago,[54-56] their study and practical utilisation were not resumed until the end of the 1960's and the beginning of the 1970's. Numerous communications devoted both to the study of the CT and cocyclotrimerisation reactions of isocyanates[57-117] and to the synthesis of various materials based on them[1-53] have now been published. The majority of the studies concerning the CT reactions were undertaken to investigate the efficiency of various kinds of catalysts in this process; many fewer studies have dealt with the reaction kinetics and mechanism. The data published in the above communications are frequently contradictory. At the same time the great interest in this process, associated with the practical possibilities for its utilisation in the formation of new materials, requires the analysis and survey of the data concerning it which have now accumulated. The existing reviews[8,41-43,58,62,63,118-129] do not contain sufficiently complete information about this question.

The cyclotrimerisation of isocyanates in the absence of a catalyst takes place slowly at 373 K. In order to carry it out under milder conditions and to ensure process selectivity, a large assortment of both acid and basic catalysts is used at the present time. The acids are fairly weak catalysts of the above process and are effective only at elevated temperatures.[41,130] The basic catalysts of the cyclotrimerisation of isocyanates known at the present time are tertiary amines,[5,12,15,32,50,59,84,95,100,115,131-138] phosphines and phosphites[5,96-98,139,140] metal alkoxides,[95,102,142,141-144] metal carboxylates[4,5,9,56,59,60,62,82,83,101,102,108,109,115,118,125,145,146] metal oxides,[77,110] quaternary ammonium bases as well as their alkoxides and carboxylates[8,95,147-150] hydrides,[111] cobalt, iron, and tin acetylacetonates,[79,80] organometallic compounds,[61,112,113,145,146,151-154] combined catalysts (amine/epoxide, amine/aldehyde, amine/imine, amine/alkylene carbonate, amine/alcohol, amine/epoxyalkane/proton donor, amine/carboxylic acid, amine/metal carboxylate, amine–organometallic compound, alkali metal carboxylate/oligoether, and amine/metal alkoxide),[6-8,21,25,29,31,34,45-50,74,88,91-95,104,116,118,120,128,150,155-160,161-171] and other catalysts (aminoimides, sulphonium zwitter-ions, alkali metal salts of aminoacids and glycine amide, as well as their combinations with other catalysts).[24,172-179] Among the entire enormous assortment of the catalysts quoted, alkali metal and alkaline earth metal carboxylates, quaternary ammonium carboxylates (and also alkoxides or phenoxides), certain tertiary amines, namely mono- di- and tri-substituted dialkylaminoalkylphenols and *NN'N"*-tri(dialkylaminoalkylene)-*sym*-hexahydrotriazines, as well as certain combined catalysts and catalytic systems are at present of greatest practical importance.[8,10-40,45,46,128,148-150,161-168,180-182]

II. CATALYSIS BY TERTIARY AMINES AND CATALYTIC SYSTEMS BASED ON THEM

The relative catalytic activities of various tertiary amines in the CT reaction of isocyanates have been estimated.[50,95,136] A number of investigators have noted in this connection that, in the presence of aliphatic or alicyclic tertiary amines, the formation of cyclic trimers from isocyanate is observed only

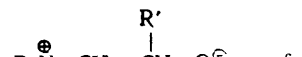
at elevated temperatures.[84,137] Even in the presence of an amine active in the urethane-formation process, such as triethylenediamine (TEDA), the formation of only the phenyl isocyanate (PIC) dimer has been observed.[94] In the presence of an alcohol or a urethane and an amine, an increase of the yield of the trimer has been noted, which led Kogan to propose a mechanism for the cyclotrimerisation of an isocyanate in a system of this kind via the formation of a dimer and allophanate:[84]

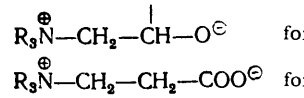
$$PhNCO + C_2H_5OH \begin{cases} \xrightarrow{\sim 293\ K} PhNHCOOC_2H_5; \\ \xrightarrow{398\ K} PhNHCON(Ph)COOC_2H_5 + (PhNCO)_2; \\ \xrightarrow[398\ K]{amine} (PhNCO)_3 + PhNHCOOC_2H_5. \end{cases}$$

Subsequent studies have established, however, that the formation reaction of the isocyanate dimer is independent of the CT process[62,79] and that the formation-dissociation reaction of the allophanate is coupled with the CT process.[50]

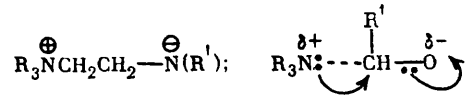
The most active tertiary amines in relation to the CT reaction of isocyanates proved to be mono-, di-, and tri-(dialkylaminoalkyl)phenols as well as symmetrical tri(dialkylaminoalkyl)hexahydrotriazines, which have found fairly extensive applications in real processes designed to synthesise polyisocyanurate-containing materials.[31-40] Early investigations[92,94,95] already established, however, that compounds such as olefin oxides, aldehydes, alkyleneimines, and 2-methylimidazole are effective cocatalysts of the CT reaction of isocyanates in the presence of tertiary amines. It has been shown[80] that ethylene carbonate and β-propiolactone can function as cocatalysts in analogous systems and alkylene sulphides have also been used for this purpose in other investigations.[72,73] Ketones (isobutyl methyl ketone and acetone), ethers (dioxan, tetrahydrofuran, and the dimethyl ether of diethylene glycol), esters (ethyl acetate), as well as acrylonitrile do not activate appreciably the CT reaction of isocyanates in the presence of tertiary amines,[94] although subsequently the acceleration of the CT reaction of 2,4-tolylene diisocyanate (2,4-TDI) in the presence of a number of ethers, including epoxides, was observed.[134,136] However one should note that in this case ethers behaved more like a second solvent (they were introduced in a large excess relative to 2,4-TDI), influencing the properties of the medium and the specific solvation of the reactants. The data in Table 1 as well as the efficiencies of various types of catalysts in the CT reaction of isocyanates, quoted by Behrendt and Joel,[50] show that, in the presence of an epoxide, the catalytic activities of all the amines investigated increase. The basicity of the amine is not then the only decisive factor; the process is also influenced by the structure of the substituents at the nitrogen atom.[136]

The relative efficiences of all the cocatalysts in the CT reaction of phenyl isocyanate in the presence of triethylenediamine have been estimated[94] and it has been established that low-molecular-weight olefin oxides and aldehydes are much more effective cocatalysts than their higher homogogues. The cocatalytic activity series of olefin oxides has been established: epoxyethane > epoxypropane > epoxybutane > epichlorohydrin > styrene oxide > 1,2-epoxyhexane > 1,2-epoxyoctane. It has also been demonstrated that *N*-methylethyleneimine is itself a catalyst of the CT reaction of isocyanates, but in combination with TEDA its activity increases. This also happens when it is combined with an epoxyalkane.[94] Having estimated the dependence of the rate of the CT reaction of 2,4-TDI on the catalyst, cocatalyst, and monomer concentrations, Beitchman[92] showed that, with increase of the concentration of each ingredient of the catalytic mixture, the rate of reaction increases too and in all cases the reaction obeys a formal first order kinetic equation. By analogy with the hypothetical structures of the zwitterions formed in the CT reactions of isocyanates in the presence of tertiary amines, proposed by Jones and Savill,[88] i.e.


for the amine/epoxyalkane combination,


for amine/propiolactone,

he suggested, in discussing the possible mechanism of the observed cocatalytic effect of various compounds in the above reactions, that the catalytic structures



are active for the amine/imine and amine/aldehyde combinations. Bearing in mind the presence of an induction period in the CT reaction of an isocyanate in the presence of amine/cocatalyst systems and the absence of autocatalysis by the reaction product (the isocyanate dimer and trimer), Beitchman also suggested that the observed autocatalysis is associated with the formation of an intermediate transition compound at a constant concentration and that it may comprise a catalyst–isocyanate complex with one or two isocyanate molecules, in conformity with the following mechanism:

$$C + I \rightleftarrows CI,$$
$$CI + I \rightleftarrows CI_2,$$
$$CI_2 + I \rightleftarrows C + T,$$

where C = TEDA/cocatalyst, I = isocyanate, and T = trimer.

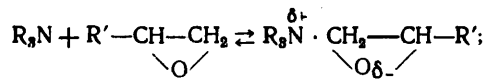
Table 1. The relative activities of tertiary amines in the cyclotrimerisation of isocyanates.[95,136]

In chlorobenzene (4 *N* PIC solution Ref.95)		2,4-TDI (0.35 mole), in bulk, in the presence of epoxypropane (0.03 mole) (Ref.136)			
catalyst	relative rate of CT	catalyst	amount of amine, mole	τ up to T_{max}, min	pK_a of amine
2,4,6-Tri(dimethylaminomethylene)phenol (I)	1.0	triethylenediamine	0.0022	6.0	8 6
(I) + diglycidyl ether of bisphenol (A) (1 : 1)	1.2	*NNN'N'*-tetramethylbutylenediamine	0.0035	30.8	10.6
NN'N''-Tri(dimethylaminopropylene)-*sym*-hexahydrotriazine (II)	2.4	pyridine	0.0025	75.0	5.29
(II) + diglycidyl ether of bisphenol (A)	7.7	*N*-methylmorpholine	0.0023	**	7.41
Triethylamine + epoxypropane	*	2-methylimidazole	0.012	**	—
2-Hydroxypyridine	*	—	—	—	—

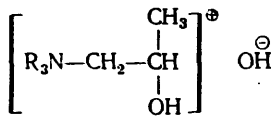
*The reaction was not observed for 30 min.
**The reaction was not observed for 120 min.

Subsequently several studies of the kinetics of the CT reactions of isocyanates in the presence of an amine/epoxide system, which were also designed to elucidate the role of the cocatalysts and the possible process mechanism, were carried out.[6-8,74,120,136,155-158,163,164,168,169,183] Various hypotheses

were put forward concerning the mechanism of the catalytic action of epoxides in this system. Together with the structure of the zwitter-ion proposed previously[94] and discussed in a later investigation,[145,184] the following features were considered: the complex of the epoxide with the amine formed as a result of the partial redistribution of charges without the opening of the epoxide ring:[74]

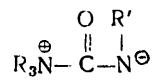


the complex of the epoxide with the isocyanate;[135,136] the product of the interaction of the tertiary amine, the epoxide, and water (traces of which are as a rule present in the catalytic systems):[6,8,94]



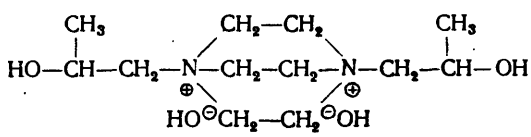
(III)

the complex of 3C* with the isocyanate trimer, where C* is a compound with an active centre initiating the CT reaction of the isocyanate, which can consist either of a zwitter-ion or a product of type (III).[120,155–158] Unfortunately, none of the proposed structures has been demonstrated experimentally. However, it has been confirmed quantitatively that, in the presence of an amine/epoxide system, the rate of cyclotrimerisation of isocyanates varies in proportion to the change in the concentrations of both ingredients,[74] although it has been shown[136] that the proportionality between the rate of the CT reactions of isocyanates and the epoxide concentration is not maintained in all solvents. On the basis of this factor and bearing in mind also the negative result of the Auerbach test for the presence of quaternary ammonium compounds and the constant content of the epoxy-groups in the course of the reaction, the authors explain the cocatalytic effect of epoxides (as well as that of several ethers) by the formation of a complex with the isocyanate. The proposed mechanism of the catalysis of the given reaction presupposes the direct interaction of the tertiary amine with the isocyanate to form a zwitter-ion having the following structure:[135,136]



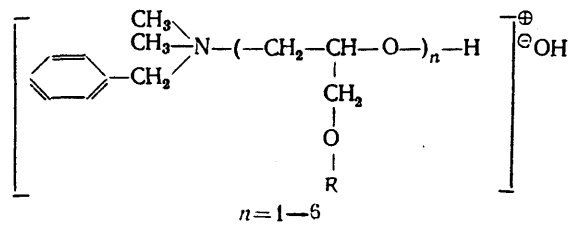
However, one should note that the constant concentration of epoxy-groups in the course of the CT reaction is not apparently an unambiguous indication that there is no possibility of interactions in the system involving the opening of the epoxide ring and the formation of active products, because the concentration of the latter may be extremely low compared with the initial concentration of the epoxide.

The hypothesis of the possible formation of a product of type (III) in the amine/epoxide catalytic system was put forward in an early study by Beitchman,[94] who showed that the product of the interaction of TEDA, epoxypropane, and water, for which he proposed the structure



is an effective catalyst of the cyclotrimerisation of TDI. In the case where TEDA and epoxypropane were thoroughly dried and the CT reaction was carried out in a tube *in vacuo*, the formation of a trimer was not observed over a period greater than 4.5 h. Taking this finding into account, the author presumes that the presence of traces of moisture in the amine/epoxide catalytic system is essential for the formation of an active catalytic complex. However, the CT reaction of the isocyanate in the presence of a product of type (I) retained an induction period,[94] which is evidence that the formation of this product is not a sufficient condition for the effective initiation of the process.

In later studies[6,8] it was also shown that under conditions excluding the access of moisture to the dimethylbenzylamine/glycidyl phenyl ether catalytic system, the CT reaction of 2,4-TDI is not observed. These workers also noted the disappearance of epoxy-groups in the interaction of equimolar amounts of benzyldimethylamine, glycidyl phenyl ether, and water. The appearance of the absorption band due to the hydroxy-group was then noted in the infrared (IR) spectrum. The authors proposed the following structure for the products isolated under these conditions:



$n = 1—6$

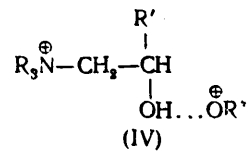
It was shown that their catalytic activity in the CT reaction of 2,4-TDI and poly(diene diisocyanates) is much greater than the catalytic activity of the amine/epoxide binary system. However, here too the reaction had an induction period. The comparatively high catalytic activity of quaternary ammonium hydroxides in the CT reaction of isocyanates had also been noted earlier.[95] In connection with the results described, catalysts of this kind at one time found practical application in the synthesis of polyisocyanurate materials.[148,149,181,185–187]

The dependence of the rate of the CT reaction of isocyanates on the preliminary contact time between the components of the amine/epoxide system has been reported.[188] In the same communication it is also noted that the presence of a third component—a proton donor—is essential for the formation of an active intermediate compound in the above system. Subsequently it was observed[182] that the interaction of tertiary amines (TEDA, etc), epoxyalkanes, and proton donors (PD) such as alcohols, phenols, or any other compounds with a mobile hydrogen atom (urethane, allophanate, urea, and biuret)[150,189] lead to products of the type of alkoxides (phenoxides) of quaternary ammonium bases, which are much more active catalysts of the cyclotrimerisation of isocyanates than the initial binary catalytic systems and are more active than adducts based on tertiary amines, epoxides, and water.

The dependence of the kinetics of the CT reaction of an isocyanate on the duration of the preliminary interaction of the components of the amine/epoxide and amine/epoxide/PD catalytic systems and also on the type of PD was first investigated in several studies.[163,164,168,190] In the investigation of the kinetics of the CT reaction of phenyl isocyanate

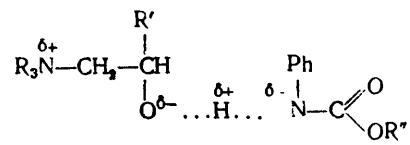
in chlorobenzene in the presence of the 2-methyltriethylenediamine/glycidyl phenyl ether (GPE) catalytic system, it was established that, with increase of the preliminary contact time between the components of the catalytic system and also with increase of its moisture content, the rate of the CT reaction of phenyl isocyanate increases while the induction period shortens.[163,168,190] It has also been observed that, after the preliminary interaction of the amine, the epoxide, and PD such as alcohols and phenol, the activity of the catalytic system investigated in the CT reaction of an isocyanate increases by more than two orders of magnitude, while the induction period is sharply reduced under these conditions. The interaction then terminates after 2–48 h depending on the reaction conditions, the reactant concentrations, and the type of PD, while the active adducts formed are stable during storage in the absence of moisture. It has been observed in addition that the products of the primary and secondary reactions of an isocyanate with alcohol or water (urethane, allophanate, urea, and biuret) can also play the role of active PD in the catalytic system investigated.[163,168] The character of the dependence of the rate of the main reaction and of the reciprocal of the induction period on the treatment time (and hence on the activity) of the amine/epoxide/PD catalytic system is identical in all cases, which indicates the decisive role of the initiation stage in the overall process kinetics. It has also been shown that the duration of the induction period and the rate of reaction depend on the concentration of each of the three components of the catalytic system, i.e. the involvement of all three components is obligatory for the formation of the active products. In the presence of carefully purified components of the amine/epoxide binary mixture the CT reaction of phenyl isocyanate was not observed for several hours.[168] Subsequently the authors studied in detail the role of the PD in the catalysis of the CT reaction of isocyanates by the amine/epoxide system.[150] It has been established by argentimetric titration[150,168] that the concentration of the epoxy-groups decreases with time in the 2-methyl-TEDA/epoxide/PD system; the rate of change of their concentration increases with increase of the amount of PD and when methanol is replaced by phenol. It has been established by dielectrometric and potentiometric titration methods[150,163] that the epoxy-rings are opened during the interaction in the 2-methyl-TEDA/epoxide/PD system and 1:1:1 molecular complexes are formed, their polarity being greater than that of the initial components and their basicity being at the level of that of quaternary ammonium bases. According to IR spectroscopic data,[164,169] the above interaction is accompanied by appreciable changes in the PD structure, particularly by an intense ionisation of the O–H and N–H bonds respectively. Thus it has been shown that the role of the PD in the catalytic system investigated consists in the fact that it is capable of opening the epoxide ring in the presence of a tertiary amine and forms part of the composition of the product—the active catalyst of the CT reaction of isocyanates.

Analysis of studies in the field of the polymerisation of epoxy-compounds in the presence of tertiary amines and alcohols[191–200] which are, in principle, not associated with the cyclotrimerisation of isocyanates but are devoted to the investigation of the interaction in ternary amine/epoxide/alcohol systems, has shown that products of the type of tertiary ammonium alkoxides (phenoxides), which are in fact the effective catalysts of the polymerisation of epoxides, are formed in such systems. Studies in this field[197–199] have shown that the interaction in the amine/epoxide/alcohol system entails the disappearance of epoxy-groups and the appearance of hydroxy-groups with an absorption band at 3280 cm^{-1}, which have been identified[195] as the OH groups in the catalytic complex having the following structure:



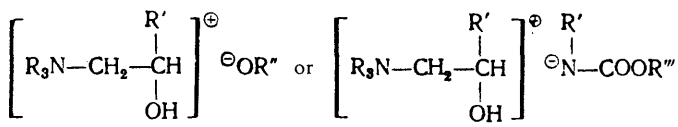
(IV)

The rate of interaction in the amine/epoxide/alcohol system does not depend directly on the basicity of the amine but is to a large extent determined by the steric structure of the latter.[136] It has been suggested[150,168] that analogous reactions take place in the catalytic systems for the cyclotrimerisation of isocyanates based on amines and olefin oxides in the presence of a proton donor. The structure of the products formed in the case of an alocohol as the proton donor is then assumed to be analogous to that of complex (IV) and in the case of a urethane as the proton donor the product is believed to be a complex having the following structure:



(V)

The study of the probability of the formation of donor–acceptor complexes in the amine/epoxide/PD system by the semiempirical quantum-chemical LCAO-MO SF method in terms of the CNDO/BW approximation has shown[201] that compounds of types (IV) and (V) should be formed as transition compounds in the formation of ionic tetraalkylammonium compounds:



(VI) (VII)

It has been established[150,183] that the concentration of adducts of types (VI) and (VII) is proportional to the rate of trimerisation of PIC (the partial order of the reaction with respect to the catalytic adduct is unity). In this case the adduct based on urea proved to be the most active. The adduct based on phenol also showed an enhanced activity. The increase of activity on passing from water and methanol to phenol can be accounted for by the increase of the polarity and basicity of the catalytic adduct formed.[150] The relatively high catalytic activity of the system based on urea can apparently be explained by the fact that water and the products of its interaction with isocyanate exert different influences on the processes investigated, depending on their concentration in the system. In small amounts, they can behave as effective PD cocatalysts, while an increase in their concentration can lead to an appreciable decrease of the rate of cyclotrimerisation of isocyanates.[8,144]

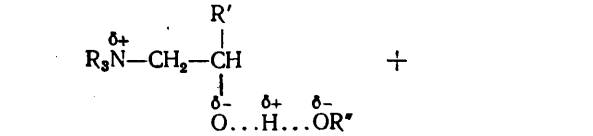
In a weakly polar solvent (for example in chlorobenzene) the form of the kinetic curves for the cyclotrimerisation of PIC in the presence of compounds of the type of quaternary

ammonium alkoxides corresponds to a quasi-unimolecular first-order reaction up to a conversion of ~90% with an induction period whose duration is determined by the concentration and structure of the catalysts. At the end of the induction period, the rate of reaction is close to the maximum value and the concentration order with respect to the monomer is then two.[150]

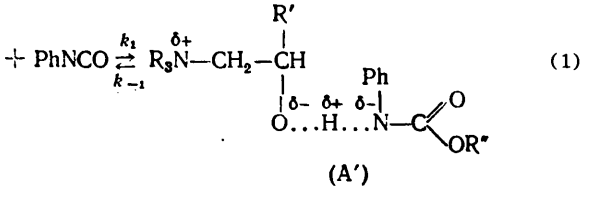
The kinetics of the cyclotrimerisation of isocyanates in the presence of basic catalysts are significantly influenced by acid inhibitors.[150] Presumably, the induction period in the reaction investigated is determined by two factors, namely by the action of the inhibitor and by the slow initiation.

According to the results obtained, the hypothetical process mechanism proposed by Zhitinkina et al.[168] is as follows (Scheme 1):

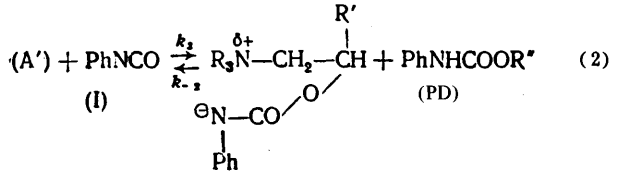
Scheme 1



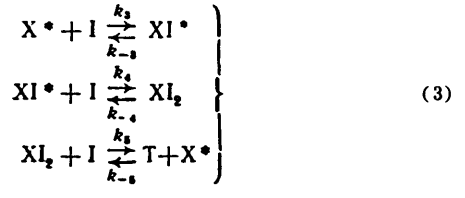
(A)



(A′) (1)



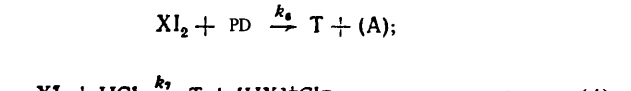
(X*) (2)



(3)

where X* is the initiator.

According to this scheme, the interaction during the induction period between the catalyst and the isocyanate leads to the formation of the initiator X*, which is much more active than the initial catalyst. Stage (2) can then apparently include also more complex interactions between the initial catalytic complex and the isocyanate (or the products of their reactions). On the other hand, when the initial catalyst, obtained from a tertiary amine, an olefin oxide, and a urethane, is used as a proton donor, the process must be regarded as starting with stage (2). The chain termination in stage (3) can then occur as a result of the proton donor present in the system or other impurities (mainly acid ones), for example, HCl:

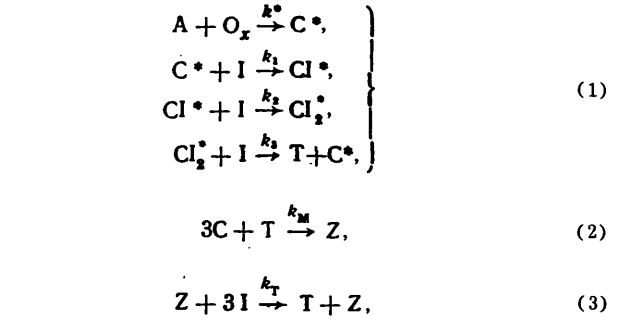


(4)

However, Korzyuk et al.[169] were not able to establish a correlation between the rate of cyclotrimerisation of the isocyanate and the concentration of the quaternary ammonium catalyst. In their study of the kinetics of the cyclotrimerisation of PIC in a mixed solvent (chlorobenzene/dimethyl sulphoxide) by IR spectroscopy, they observed that the reaction consists of two stages and begins under conditions without an induction period. The proportionality between the catalyst concentration and the rate of formation of the trimer is then observed only for the first stage of the process. According to the authors, the observed two-stage nature of the reaction is associated with the rearrangement of the catalyst during the reaction. However, presumably in the systems investigated the anomalous kinetics can be due to the possible interaction of the monomer with dimethyl sulphoxide.[145,146,154]

In the series of studies devoted to the kinetics of the cyclotrimerisation of isocyanates in the presence of an amine/epoxide catalytic system (CS), a special place is occupied by a number of investigations.[120,155–158] In their study of the kinetics of the cyclotrimerisation of *m*-chlorophenyl isocyanate (*m*-Cl-PIC) in dioxan in the presence of the epoxypropane/triethylenediamine catalytic system, the authors found that the trimer obtained in the presence of the TEDA/epoxypropane catalytic system accelerates the cyclotrimerisation of the isocyanate (in contrast to the trimer obtained in the presence of TEDA alone). When it is introduced into the reaction mixture simultaneously with the catalytic system, the trimer does not accelerate the reaction, while, after it has been kept together with the catalytic system beforehand, it does accelerate the cyclotrimerisation of *m*-Cl-PIC and shortens the induction period. From these findings and also taking into account the fact that they found the order of the reaction to be 1–3 with respect to the active centre C* and 2.6 with respect to the monomer, the authors proposed a template mechanism of the catalysis of the cyclotrimerisation of isocyanate. According to this mechanism, the trimer formed plays the role of a template on which three active centres are grouped. This structure of the template catalyst is believed to enable the simultaneous coordination of three isocyanate molecules on the catalyst. Thus the process proceeds via the mechanism (Scheme 2)

Scheme 2



(1)

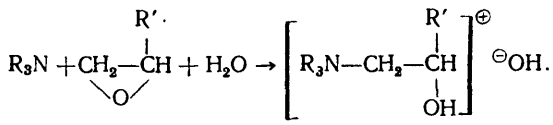
(2)

(3)

where A is the amine, O_x the epoxyalkane, and C* the active centre. The first stage is the formation of the trimer (seed) and the second stage involves the formation of the template catalyst Z, capable of rapidly coordinating three monomer molecules with formation of the final product.

The modelling of the proposed kinetic scheme on an analogue computer makes it possible to attain qualitative agreement between the principal calculated and experimental features of the reaction kinetics. The authors believe that the set of data which they obtained for the CT reaction of isocyanates definitely constitutes evidence in support of the view that a reactive product is formed on a catalyst of the template type consisting of the trimer molecule containing three active centres.[120,155-158]

However, one should not fail to note certain contradictions concerning the proposed mechanism. In the first place the accelerating role of the trimer in the cyclotrimerisation of isocyanates has not been confirmed in a number of studies.[94,136,137,147,150] One of the main features identifying the operation of the proposed mechanism is believed[158] to be a reaction order ranging from 1 to 3 with respect to C*. However, in order to calculate the concentration of C* at the instant of the reaction, the authors employ the effective rate constant k_{eff} for the formation of active centres from the amine and the epoxide, obtained by extrapolating the constants k_{eff} characterising the rate of the above reaction in aqueous dioxan to pure dioxan. In their study of the kinetics of the formation of active products from TEDA and epoxypropane (EP) in aqueous dioxan, the authors assume that the role of water in this process consists in altering the dielectric constant of the medium and in the possible solvation of the reactants (TEDA). On the other hand, the studies on the reactions occurring in the polymerisation of epoxides[191-200] and also other investigations[6,163,168,201] permits at the present time the unambiguous claim that the interaction in the amine/epoxide system with opening of the epoxide ring does not take place at all in the absence of at least traces of a PD. Water is an effective PD in systems of this kind and participates directly in the reaction, entering into the composition of the product (like alcohols and other PD):



When account is taken of this finding, one should apparently exercise cuation in using the k_{eff} obtained by means of the extrapolation described above, particularly in relation to a reaction system containing an isocyanate and possible active admixtures (for example, water and urea). The rate of accumulation of active centres in such a system is probably determined not only by the concentrations of the epoxide and the amine but also by the presence of a third coreactant, the participation of which is obligatory for the formation of active centres with the opening of the epoxide ring.[6,150,163,168]

It follows from the experimental data[158] that the preliminary maintenance of the trimer in contact with the TEDA/EP catalytic system leads merely to a decrease of the induction period in the CT reaction of *m*-Cl-PIC but not to its disappearance. At the same time, it appears evident that, on formation of a template catalyst under these conditions, the reaction should begin without an induction period.

On the other hand, it is known that, under certain conditions (temperature, catalyst), the stable isocyanurate ring can be cleaved on treatment with epoxides to form 2-oxazolidinones.[202] One cannot rule out the possibility that the observed effect of the trimer in the given process[120,155-15] is associated with reactions of this kind.

Naturally one of the confirmations of the template mechanism of the CT reaction of isocyanates may be the experimental detection of a complex catalyst of the template type.

Quantum-chemical calculations by the LCAO-MO SCF method in terms of the CNDO/BW approximation have shown that the structural characteristics of the components of the amine/epoxide catalytic system and of the trimer indicate a low probability of the formation of a template catalyst owing to steric hindrance.[201]

III. CATALYSIS BY TIN, ZINC, ANTIMONY, PHOSPHORUS, AND ARSENIC COMPOUNDS AND METAL NAPHTHENATES AND ACETYLACETONATES

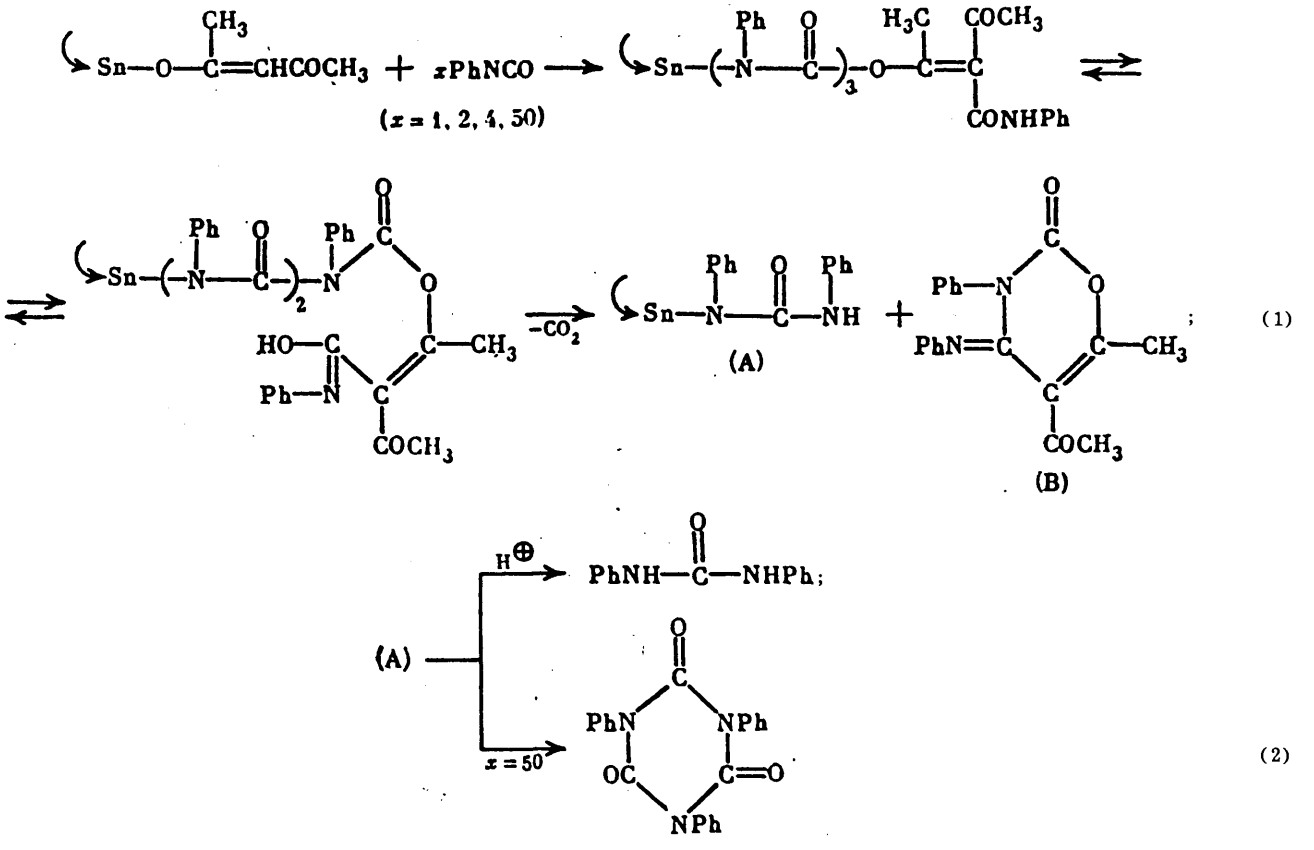
Virtually all the studies on the above types of catalysts[61,77-80,118,145,146,151-155] involved merely an estimate of the catalytic activity of compounds of this kind in relation to the cyclotrimerisation of isocyanates and certain ideas about the mechanism of this reaction under the conditions investigated. A distinctive feature of all the proposed mechanisms of the CT reaction of isocyanates in the presence of such catalysts is catalysis with the aid of "insertion" reactions.[61]

The catalytic activity of antimony and arsenic trialkoxides in the cyclotrimerisation of isocyanates has been reported.[77] In the presence of antimony tri-n-butoxide and arsenic triisobutoxide, the authors obtained high yields of the trimers of PIC, *o*-methoxyphenyl and ethyl isocyanates, hexamethylene diisocyanate, and *m*-nitro- and *m*-chloro-phenyl isocyanates. It was also observed that tri-n-butylantimony diethoxide and triisobutylantimony diacetate as well as the dioxides are active catalysts of the cyclotrimerisation of isocyanates. The more basic oxides of trialkylantimony and trialkylarsenic showed a higher catalytic activity in the cyclotrimerisation of isocyanates. The author suggested that catalysis by the test compound entails the initial formation of a stoichiometric complex of the isocyanate with the catalyst, which subsequently reacts with the excess isocyanate to form the trimer. The suggested complex has been isolated after the reaction of antimony tri-n-butoxide with a slight excess of PIC and has been characterised in terms of its elemental composition and by IR spectroscopy. The product exhibited a catalytic activity in the cyclotrimerisation of the isocyanate.

The cyclotrimerisation of 2,4-TDI in the presence of iron acetylacetonate as the catalyst has been observed.[79,80] The author showed that the dimerisation of the isocyanate is in this case an independent process. It was found that the initial rate of dimerisation decreases from the maximum value almost to zero at the equilibrium concentration of the dimer and the trimerisation process under these conditions does not correspond to equilibrium, the activation energy amounting to 44.2 kJ mol^{-1}.

In their study of the reaction of PIC in the presence of β-dicarbonyl complexes of tin, Wakechima et al.[151] proposed a mechanism of the catalysis involving "insertion" reactions, i.e. with insertion of the isocyanate in the Sn–O bond (Scheme 3). The products formed under these conditions in the first stage can undergo various transformations depending on the $PhNCO/Sn(acac)_2$ ratio:

Scheme 3



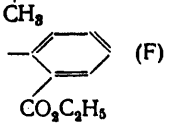
(1)

(2)

The occurrence of "insertion" reactions in the cyclotrimerisation of isocyanates in the presence of catalysts containing the Sn–S and Sn–O bonds (oxides and alkoxides) has been indicated in several studies.[61,155,203] In their investigation of the cyclotrimerisation of PIC and ethyl isocyanate in the presence of catalysts having the structure

$Sn(OR)_2$, where $R=C_2H_4N(CH_3)_2$ (A);

$C_2H_4OCH_3$ (B); C_2H_5 (C); $C(CH_3)=CH-COCH_3$ (D);

$C(CH_3)=CHCO_2C_2H_5$ (E);  (F)

Wakechima and Kijima[152] found that these compounds are active catalysts of the cyclotrimerisation of isocyanates. The highest activity was noted for compound (A) and the lowest for compound (F). Hence it was concluded that the nucleophilic properties of the oxygen atom are important in the catalysis of the cyclotrimerisation of isocyanates by bivalent tin compounds. The above workers also showed that compounds of quadrivalent tin such as $Sn(OC_4H_9)_4$ and $n\text{-}C_4H_9Sn(OS_4H_9)_3$ hardly catalyse the cyclotrimerisation of PIC under the same conditions. In their investigation of the interaction of isocyanates with quadrivalent tin oxides and alkoxides, Tiger et al.[155] found that in their presence the isocyanate is slowly converted into the trimer. Various isocyanates can then give rise to mixed isocyanurates. Hence the authors concluded that the cyclotrimerisation in the presence of R_3SnX proceeds via the consecutive insertion of the isocyanate between Sn(IV) and the counterion (X), affording initially a carbonate and then 1 : 2 (allophanate) and 1 : 3 adducts (Scheme 4):

Scheme 4

$$(C_4H_9)_3SnX + RNCO \rightleftarrows \underset{\text{(VIII)}}{(C_4H_9)_3Sn\cdot NRCOX}; \quad (1)$$

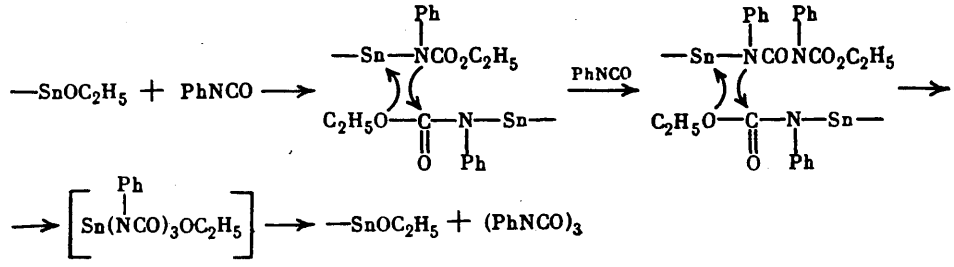
$$\text{(VIII)} + R'NCO \rightleftarrows \underset{\text{(IX)}}{[(C_4H_9)_3Sn\cdot NR'CONRCOX]}; \quad (2)$$

$$\text{(IX)} + R'NCO \rightleftarrows \underset{\text{(X)}}{[(C_4H_9)_3SnNR'CONR'CONRCOX]};$$

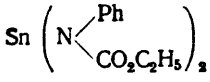
$$\text{(X)} \rightarrow (C_4H_9)_3SnX + T. \quad (3)$$

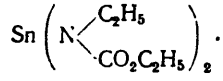
However, instances of the direct formation of a product of type (IX) could not be observed. In all cases the hydrolysis of the products yielded only the carbamate and the trimer, whence it was suggested that the allophanate reacts very rapidly with subsequent conversion into the carbamate.

In contrast to this, the mechanism of the catalysis of the cyclotrimerisation of isocyanates by bivalent tin compounds, involving the four-centre intermolecular interaction



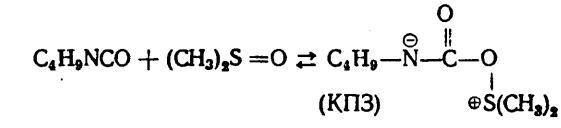
has been proposed[152] on the basis of the change in the yield of the hydrolysis products. The authors believe that the proposed reaction pathway is confirmed by the weakening of the nucleophilic attack by the nitrogen atom in



compared with  .

Two groups of catalysts in the cyclotrimerisation of aromatic and aliphatic isocyanates have been investigated:[145,146,154] the first group $[(C_4H_9)_3Sn]_2O$, $Ti(C_4H_9)_4$, and $Zr(OC_4H_9)_4$, while the second includes lead, zirconium, and cobalt naphthenates. It was shown that the catalysts of the first group are effective in the cyclotrimerisation of aromatic isocyanates and are almost ineffective in that of aliphatic isocyanates. The addition of polar solvents [dimethylformamide(DMF) and dimethyl sulphoxide(DMSO)] to the isocyanate in proportions of 1 : 1 leads to a sharp acceleration of the cyclotrimerisation of PIC in the presence of catalysts of the first group, while in the presence of those in the second group the cyclotrimerisation of PIC is accelerated even after the addition of a small amount of DMF or DMSO. In the case of C_4H_9NCO the addition of polar solvents hardly accelerates the cyclotrimerisation in the presence of catalysts of the first group. On the other hand, the addition of small amounts of, for example, DMSO leads to an appreciable acceleration of the cyclotrimerisation of C_4H_9NCO by catalysts of the second group, although the overall process remains slower than in the case of PIC. Under these conditions, there is an optimum in the rate of cyclotrimerisation of C_4H_9NCO (in the presence of catalysts of the second group) as a function of the content of DMSO in the system at the concentration of the latter 5–10 times greater than that of the catalyst.

An explanation of the observed facts follows from the consideration of complex formation in isocyanate–solvent and isocyanate–catalyst systems. It was shown[145,146,154] that, compared with PIC, C_4H_9NCO interacts only weakly with DMSO and that the concentration of the charge–transfer complex (CTC) (which is more active than the initial monomer) formed under these conditions is very low.



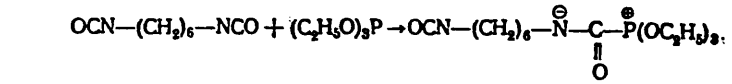
This in fact accounts for the absence of an increase in the rate of cyclotrimerisation of aliphatic isocyanates in the presence of polar solvents.

On the basis of the appreciable increase of the rate of cyclotrimerisation of isocyanates (both aromatic and aliphatic) in the presence of small amounts of DMSO in catalysis by compounds of the second group, the authors suggested that very low concentrations of the charge-transfer complex are effective in complex formation with the metal, which results in the formation of a catalytic complex of the isocyanate with the metal of the catalyst. In their study of complex formation in the isocyanate–cobalt naphthenate system by the spectrophotometric method, they found[146] that both PIC and C_4H_9NCO form a complex with the catalyst having the composition [NCO]/[Co] = 3. They demonstrated at the same time that, in the complex formation reaction with the metal, the NCO group in the aliphatic isocyanate is a much weaker ligand than that of PIC. As a result of this, in the reaction of the aliphatic isocyanate the DMF or DMSO present at high concentrations can compete with the isocyanate in the complex formation reaction with the catalyst metal, causing thereby an increase in the induction period of the CT reaction. On the other hand, in the case of PIC, which forms complexes with the catalysts of the second group much faster and with a much higher equilibrium constant, the observed rate of cyclotrimerisation is much higher under the same conditions.

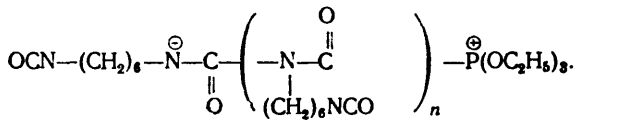
The cyclotrimerisation of organic isocyanates in the presence of organozinc compounds ($RZnNR'_2$ or $RZnOR'$) has been described.[113] Davydov et al.[106] and Cherednikova[118] investigated the cocyclotrimerisation of chlorohexyl isocyanate (CHIC) and PIC in the presence of zinc octanoate in toluene at 353–383 K and showed that CHIC is more reactive than PIC. The kinetic cyclotrimerisation curves were S-shaped: the rate of reaction increased to a maximum at the end of the induction period and then began to decrease slowly (for 30–50% conversion of the monomer). The results were interpreted by the authors from the standpoint of the template mechanism of catalysis, although the accelerating role of the PIC trimer had been demonstrated only after it had been kept in contact with the catalyst at 353 K. The formation of a stable complex of the catalyst with the PIC trimer under the conditions indicated is unlikely.

The catalytic action of certain phosphorus compounds on the cyclotrimerisation of isocyanates has been reported in a number of communications.[97,98,105,140] The active catalysts of this reaction are tertiary phosphines.[105] Trialkyl phosphites (TAP) are also vigorous nucleophiles which catalyse the formation of cyclic isocyanate dimers and trimers.[97,140] According to the authors, the polymerisation of diisocyanates initiated by TAP involves the nucleophilic attack by the phosphorus atom of the phosphite on the carbon atom of the

isocyanate group—the most electrophilic centre of the molecule:



This results in the formation of a dipolar ion; the addition of subsequent isocyanate molecules is to the anion:



The autocyclisation of the macroanion in the trimer stage can be achieved spontaneously with the regeneration of trialkyl phosphite.

IV. CATALYSIS BY ALKALI METAL AND QUATERNARY AMMONIUM CARBOXYLATES

Although alkali metal and quaternary ammonium carboxylates are nowadays used perhaps most extensively in practical systems for the preparation of isocyanurate-containing polymers and various materials based on them,[10,21,25,44-47,204] there have been comparatively few studies on the kinetics of this process and on its mechanism in the presence of catalysts of this kind.[9,62,101,102,125,128,147,161,166-168,205,206] Until recently it was believed that alkali metal carboxylates are weak catalysts of the cyclotrimerisation of isocyanates and are effective only at elevated temperatures.[136] They were therefore used most often in combination with other catalysts of the cyclotrimerisation of isocyanates.[21,25]

The characteristics of the cyclotrimerisation of aromatic isocyanates have been investigated in relation to PIC in solution in DMF in the presence of lithium acetate.[9,62,108,109,125] The conversion of PIC into a trimer took place over a period of ~3 h at 333 K. It was established that the reaction is of second order with respect to the isocyanate and of first order with respect to the catalyst. In the initial stages of the reaction, the authors observed, together with the formation of the trimer, the formation of the PIC dimer (as an independent parallel process), which at the end of the reaction was fully converted into the trimer. It has also been shown that the PIC dimer in solution in DMF at 333 K reacts rapidly to form the trimer when the reaction is catalysed by lithium acetate. The authors suggest that the interaction of the PIC dimer with lithium acetate entails the formation of catalytically active compounds capable of converting the dimer into the monomer and the trimer.[62,125] On the grounds of general considerations, the authors suggest that the active centre in the CT process is in this case the product of the addition of PIC to lithium acetate, i.e. the lithium salt of a substituted urethane.[62]

Tne cocatalytic effect of linear oligoethers in the cyclotrimerisation of isocyanates in the presence of alkali metal acetates (alkoxides, phenoxides) has been observed,[45] and it has been suggested that it be used in the synthesis of isocyanurate-containing foam plastics. Subsequently the same workers carried out a series of studies on the kinetics of the CT reaction of isocyanates in the presence of alkali metal acetates in various oligoethers and also of their low-molecular-rate analogues (glymes) as cocatalysts[44,128,161,162,165,190,206] and of the complex formation reaction in alkali metal acetate/oligoether (or glyme) systems.[44,167,168] They also carried out investigations designed to elucidate the role of oligoethers in the catalysis of the CT reaction of isocyanates by alkali metal acetates.[128,161,165,168]

The cocatalytic effect of compounds containing the ether linkage (diethylene glycol, triethylene glycol, and polyoxypropylenetriol with a molecular weight of ~3000) in the CT reaction of isocyanates (2,4-TDI) in the presence of potassium acetate as the catalyst was characterised quantitatively for the first time by Medved' and co-workers.[161,162] It has been shown that the activity of the AcOK/cocatalyst catalytic systems depends on the concentrations of both the catalyst and the cocatalyst and also on the equivalent ratio [−O−]/[AcOK]. With increase of this ratio, the rate of the CT reaction increases, while the induction period diminishes. Taking into account the data obtained for the heat of reaction of AcOK with the polyoxypropylenetriol (~21 kJ mol^{-1}; AcOK), the authors put forward the hypothesis that the observed cocatalytic effect of linear oligoethers in the process investigated is due to the specific solvation of the potassium ion by the polyether (analogously to the reaction of glymes and cyclic polyethers, namely crown-ethers, in solutions of alkali metal salts),[207-214] as a result of which the catalyst can pass from the state of contact ion pairs to one of solvate-separated ion pairs, whose activity is much higher, for example in relation to the anionic polymerisation of various monomers.[215-226]

In subsequent investigations[44,128,165,166,168,227-229] more detailed studies were made of the influence of various oligoethers on the kinetics of the CT reaction of 2,4-TDI[44,165,166,168] and of the nature and structure of the complexes formed in the AcOM/oligoether systems (where M = alkali metal).[128,227-229] It was established that AcOK in the form of solutions in methanol or ethylene glycol behaves as a very weak catalyst of the cyclotrimerisation of 2,4-DTI under the conditions investigated (298 K, in bulk) (the reaction was not observed in the course of at least 2 h).[168] The addition of even small amounts of polyethers based on epoxyethane (EE) or epoxypropane leads to a sharp increase of the rate of reaction (the process takes place over a period of several minutes). The study of the kinetics of the cyclotrimerisation of 2,4-TDI in the presence of the AcOK/polyether catalytic system established that the dependence of the rate of reaction on the equivalent ratio [−O−]/[AcOK] is represented by curves with saturation [a plateau] for a specific value of [−O−]/[AcOK], which depends on the structure and molecular weight of the polyether. It was established that oligoethers based on EE are much more effective cocatalysts in the process investigated than oligoethers based on EP; the effectiveness of the catalyst is also influenced by the molecular weight and functionality [the number and nature of functional groups (Translator)].[128,166,168] Dimethyl ethers of glycols (glymes) also accelerate the cyclotrimerisation of isocyanate in the presence of AcOK, but their activity is lower than that of their analogues having higher molecular weights—linear oligoethers based on EE (Table 2).[128,168]

According to Gerard et al.[213] and Davydova et al.,[230] the relative capacities of various compounds containing ether linkages for complex formation with alkali metal salts (NaCl, KI, CsCl) decrease in the sequence dibenzo-18-crown-6 > poly(ethylene oxide) (MW ≅ 18 000) > glyme 8 > glyme 7 > glyme 6 > glyme 5. On formation of complexes of the ligands considered with metal cations, appreciable heat changes are observed;[230] the entropies are then in most cases negative and reflect the restriction of the mobility of the ligand molecules. An important feature of the complex formation reaction of polyethers with metal salts is the decrease of the electrostatic interaction between the counterions, as a result

of which the ions are separated.[128] Since the majority of ionic catalysts are present in the polymerisation mixture in the form of ionic associated species and contact ion pairs, coordination to polyethers converts them into solvate-separated ion pairs or free ions. At the same time it is known that the catalytic activity of separated ion pairs in ionic polymerisation is higher by 2–5 orders of magnitude than that of contact ion pairs[215] and is close to the activity of free ions. Instances of the employment of glymes and cyclic polyethers as activators in the polymerisation of styrene,[216] α-methylstyrene,[217] propylene sulphide,[218] olefin oxides,[219] lactones,[220] butadiene,[215] and certain other monomers are known.

The study of the complex formation reaction between AcOK (in solution in methanol) and various linear oligoethers and glymes by calorimetric and conductimetric methods established[128,167,168] that, at a concentration in excess of 0.1 M, AcOK is present in methanol in the state of contact ion pairs and their aggregates. The addition of oligoethers to dilute AcOK solutions (10^{-3}–10^{-4} M) decreases their limiting equivalent conductance, which is a consequence of the increase of the bulk of the potassium ion and the decrease of its mobility as a result of its coordination to the polyether (the Stokes radius increases from 2.9 Å to 8.45 Å). The addition of oligoethers to a concentrated AcOK solution in methanol (0.5 M) entails partial separation of the ions and the disruption of the ionic aggregates, as a result of which the electrical conductivity of the solution increases somewhat. It has also been established[227–229] that linear polyethers based on EE and EP in solutions in methanol form partly dissociated coordination-saturated complexes via the donor–acceptor interaction of the oxygen in the ether linkage of the polyether with the potassium cation. The interaction of AcOK with polyethers is accompanied by a heat change, whose magnitude depends on the characteristics of the polyether: polyoxyethylenediols > polyoxypropylenediols (with the same degree of polymerisation) > polyoxypropylenetriols (with the same equivalent weight). The composition of the complexes depends on the molecular weight of the polyethers, i.e. on its content of electron-donating groups, namely ether linkages. Polyethers with a sufficiently high molecular weight (for example, MW ≥ 1000 for polyoxypropylenediols) can interact with two and more cations.[227–229] The interaction of polyethers with AcOK is characterised by comparatively low equilibrium constants:[229] for oligoethers based on EE, these values are greater by a factor of 2–3 (~250 litres per mole of AcOK) than for oligoethers based on EP (~100 litre $mole^{-1}$) with the same degree of polymerisation, which agrees with the data of other workers on the complex formation reactions of potassium thiocyanate with linear polyethers.[230]

It has been established[227] that the presence of ether linkages is a necessary but not a sufficient condition for the effective complex formation between the potassium ion and electron-donating ligands and for the corresponding cocatalytic effect of the latter in the cyclotrimerisation of isocyanates. Thus polyfurit, dioxan, and dibutyl ether do not solvate K^+ and do not accelerate the cyclotrimerisation of 2,4-TDI in the presence of potassium acetate. Evidently the solvating capacity of ligands of this kind is determined not only by their chemical structure but also by the conformation of their molecules. According to Gluck et al.,[231] the conformation of poly(ethylene oxide) is a helix with a repeat period of 19.3×10^{-10} m; in structured complexes poly(ethylene oxide) consists of a non-planar zig-zag with a repeat period of 11.75×10^{-10} m;[232] the conformation of polyfurit is a planar zig-zag, while dioxan has the chair conformation.[233] Only the first conformation ensures the possibility of the simultaneous involvement of two and more neighbouring electron-donating groups in the interaction with the metal cation by virtue of the high flexibility of the chain in poly(ethylene oxide) and poly(propylene oxide) and their polydentate structure.

The $\Delta H - \Delta S$ relation for the complex formation reactions of AcOK with polyoxyethylene and polyoxypropylene oligoethers is linear and is described by the equation[229]

$$-\Delta H = -0.36\,\Delta S + 1.85,$$

This relation is a common feature of donor–acceptor interactions.[234] The relation $-\Delta H = f\{[-O-]/[AcOK]\}$ has the form of curves with saturation for all the AcOK/oligoether systems investigated,[227,228] analogously to the situation demonstrated for the dependence of the rate of cyclotrimerisation on the same ratio [–O–]/[AcOK],[44,128,168,232] which indicates a direct relation between the complex formation reaction in the catalytic systems investigated and the catalytic activity of the latter in the cyclotrimerisation of isocyanates. This is also indicated by a number of other features common both to the complex formation reaction and to the cyclotrimerisation kinetics in the presence of the AcOK linear oligoether catalytic system: the high heats of reaction and the high equilibrium constants characterising the complex formation in the catalytic systems based on AcOK and oligooxyethylenes, compared with the catalytic systems based on AcOK and oligooxypropylenes, and the correspondingly higher catalytic activity of the former systems in the cyclotrimerisation of 2,4-TDI (Table 2), as well as the absence of interaction (and hence of the cocatalytic effect in the CT reaction) of polyfurite, dioxan, and dibutyl ether with AcOK, etc.

Table 2. Parameters of the complex formation reactions [$-\Delta H$(kJ/mol AcOK) and K_p (litre^n mol^{-n})] of various electron donors (ED) with AcOK and their cocatalytic activities in the cyclotrimerisation of 2,4-TDI.[168]

ED	MW	[–O–]/[AcOK] at V^1_{max} and ΔH_{max}	$-\Delta H$, kJ/mol AcOK	K_p, litre^n mol^{-n} [2]	Relative V_{max} for CT
Diglyme	134	—	15	42	1.0
Tetraglyme	222	20	33	66	1.4
POED-400	420	10	35	240	6.4
PEO[3]	520	10	41	260	6.7
POPD-500[4]	540	25	31	98	2.5
POPD-1000	1050	25	22	30	1.2
POPT-500	510	30	21	130	0.8
POPT-1000	1030	30	20	65	0.8

[1] V_{max} and ΔH_{max} are the maximum rates of cyclotrimerisation of 2,4-TDI and the enthalpy of complex formation respectively.
[2] n is the number of moles of the electron donor in the complex.
[3] PEO does not contain OH groups.
[4] POPD-500 was synthesised from diethyleneglycol and contains ~12% of hydroxyethyl groups.

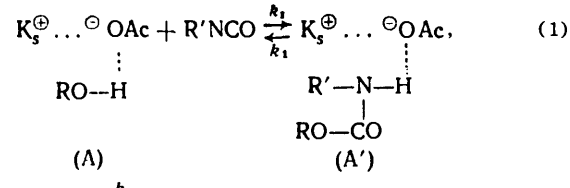
A study[235] using the potassium salts of aminoacids as catalysts of the cyclotrimerisation of isocyanates in the synthesis of isocyanurate-urethane foam plastics dealt with the principal rules governing the influence of linear oligoethers on the catalytic activity of systems, observed by

Denisov et al.[44] and Zhitinkina et al.[168] Thus, for the same content of the oligoether by weight in the composition, the replacement of oligooxyethylenediol-200 by oligooxypropylenediol-200 leads to an increase of the foaming time of the composition by a factor of 2 (from 35 to 68 s). An increase of the equivalent ratio $[-O-]/[K^+]$ diminishes the above parameter.

The cocatalytic effect of linear oligoethers based on EP and EE has been used[236] to establish highly effective catalytic systems suitable for the synthesis of isocyanurate-urethane foam plastics with effective physicomechanical parameters, thermal stability, and fire resistance.[45-47]

Analysis of data[44,128,166,168] on the kinetics of the cyclotrimerisation of isocyanates in the presence of the AcOK/oligoether catalytic systems has shown, however, that the complexes formed are not apparently the "true" initiators of this reaction, since the induction period persists (at sufficiently low catalyst concentrations). At the end of the induction period, the reaction begins at a rate close to the maximum and obeys a formal kinetic first-order equation. The order of the reaction with respect to the catalyst is unity.[168] On the basis of the factors indicated, a hypothetical mechanism of the cyclotrimerisation of isocyanates in the presence of catalytic systems of this kind has been put forward[166,168] in the following way (for systems containing ROH, Scheme 5):

Scheme 5



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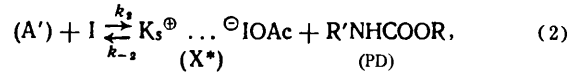

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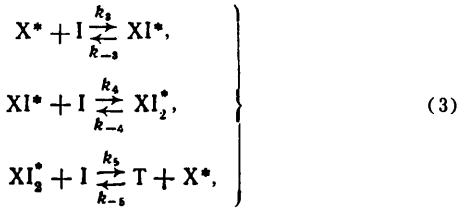
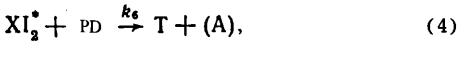
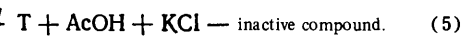


(3)



(4)

or



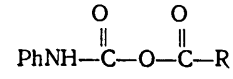
(5)

The chain termination in stage (3) of this system can apparently be due to cyclisation in the presence of a proton donor with regeneration of the initial catalyst. It is also possible that stage (2) involves more complex interactions.

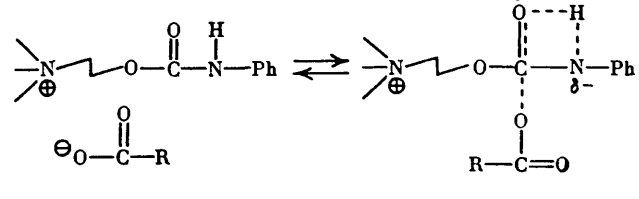
The kinetics of the cyclotrimerisation of PIC in the presence of various catalysts, including quaternary ammonium carboxylates, have been described recently.[147,205] The authors reported[205] that, in the presence of a quaternary ammonium carboxylate, the reaction is of first order with respect to the isocyanate at low degrees of conversion: at high degrees of conversion, the reaction deviates from the first order. However, in the next study[147] by the same workers involving the cyclotrimerisation of PIC in diglyme, it was stated that the reaction is of second order with respect to the monomer in the presence of a catalyst of the same type. In addition they established that the rate of reaction in the presence of a quaternary ammonium carboxylate (the DABCO TMR product) varies non-linearly under these conditions with the concentration of the catalyst and the order of the reaction with respect to the catalyst is close to two. For other types of catalysts, the order of the reaction is unity.[147] Thus fairly contradictory data have been obtained. Unfortunately, the information quoted in these communications concerning the kinetics of the cyclotrimerisation of PIC was obtained using commerical catalysts (DABCO TMR; APCI). There are no data concerning their exact structure and purity, which precludes the analysis of the results from the standpoint of the influence of various factors.

It has been established[147] that the PIC trimer does not have an accelerating effect on the cyclotrimerisation in the presence of the catalysts investigated (in the presence of the trimer, the rate of cyclotrimerisation is actually somewhat lower). The author showed that, in the presence of a quaternary ammonium carboxylate (DABCO TMR), the rate of cyclotrimerisation of PIC diminishes with increase of temperature. Since the catalyst itself does not lose its activity after being thermostatted at 323 K, they suggest that this effect is associated with the depolymerisation of the growing chain in the stages preceding cyclotrimerisation. In a study of the influence of the catalyst structure on the rate of cyclotrimerisation of PIC, Bechera[147] established that, among compounds of the given type, the catalysts with primary OH groups are more effective than catalysts with secondary OH groups while the latter are more effective than catalysts with tertiary OH groups. On the other hand, an increase of the number of OH groups in the catalyst leads to a decrease of the rate of cyclotrimerisation of PIC. It has also been established that, with increase of the basicity of the carboxylate anion, the activity of the catalyst rises, while the addition of a carboxylic acid to the catalyst reduces the rate of cyclotrimerisation of PIC. The authors do not attempt to interpret the latter fact in any way.

At a low concentration or at a low activity of the catalyst the induction period persists. In the case of substituted quaternary ammonium benzoates, its duration is inversely proportional to the basicity of the carboxylate anion. It is believed[147] that the induction period is due to the slow formation of an activated catalyst as a result of the addition of an isocyanate molecule to the OH group and that this product exhibits a somewhat higher catalytic activity than the initial catalyst in the cyclotrimerisation of PIC. In their study of the structure of the product of the addition of PIC to hydroxyethyltrimethylammonium nitrobenzoate (in equivalent proportions) by IR and NMR spectroscopy, the authors observed the presence of the absorption band of the urethane carbonyl group and the absence of free NCO groups and of the mixed anhydride of carbamic acid:

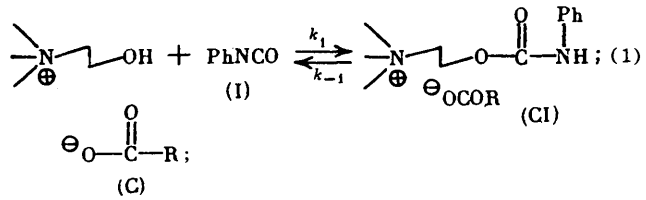


On the other hand, the presence of a very "acid" proton was revealed by the NMR spectra. On the basis of the results obtained, they represented the structure of the isocyanate-activated catalyst in the following way:

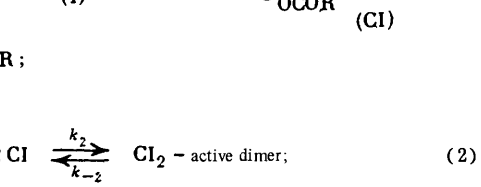


However, in an attempt to explain the observed second order of the reaction with respect to the catalyst, the authors assumed further that this product forms a very active dimer in the initiation stage and put forward the following mechanism for the cyclotrimerisation of isocyanate in the presence of ROH (Scheme 6):

Scheme 6



(1)



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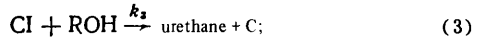

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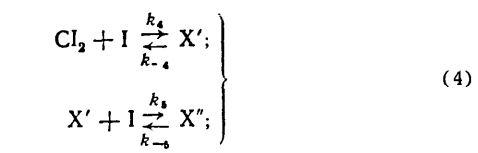

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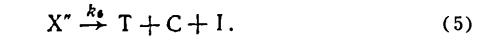
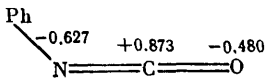


(5)

It is fairly difficult to imagine the nature of such a dimer, which was in fact stated by the authors themselves.

V. SOME FEATURES OF THE KINETICS OF THE CYCLOTRIMERISATION OF ISOCYANATES AND THE PROPOSED PROCESS MECHANISM

Isocyanates belong to the class of unsaturated compounds with cumulated double bonds,[237-240] which determines their reactivity in relation to various compounds, including their reactivity in relation to one another. The electron density in the NCO group is distributed in such a way that the nitrogen and oxygen have electron-donating properties, while carbon has electron-accepting properties. Quantum-chemical calculations of the distribution of electron density in isocyanates, carried out by the CNDO/BW method with optimised geometry, which agree qualitatively with non-empirical calculations,[241] have shown that the nitrogen atom carries a larger negative charge than the oxygen atom:

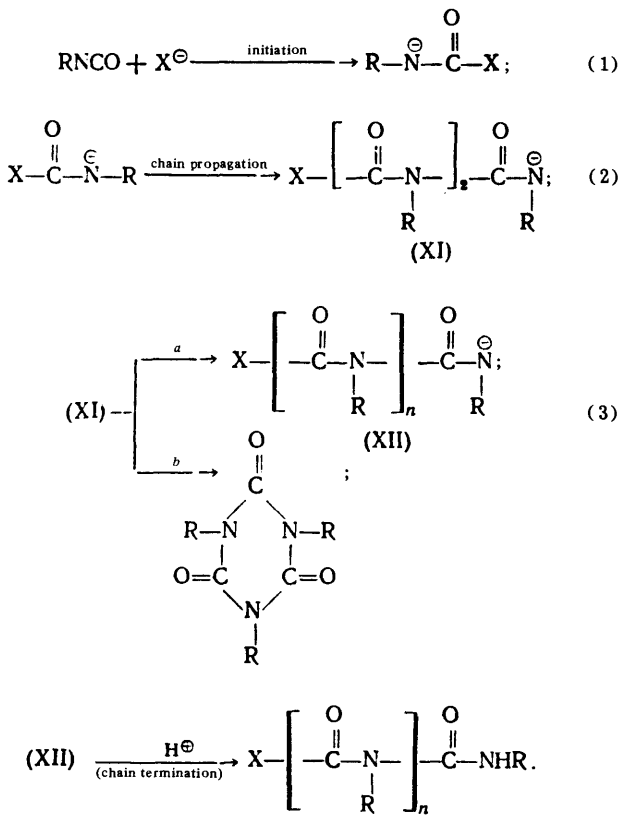


From the C=O (635 kJ mol^{-1}) and C=N (375 kJ mol^{-1}) bond energies quoted by Fedotova et al.,[242] one can assume that the addition to the N=C bonds is easier. The results of studies on the EPR spectra of the radicals formed on γ-irradiation of isocyanates and ρn their interaction with active hydrogen atoms confirm this.[243] All subsequent studies devoted to the synthesis of linear homopolymers of isocyanates,[244-247] their copolymers,[64-71] and cyclic trimers indicate the preferential cleavage of the N=C bond.

A number of studies have been devoted to the elucidation of the causes of the anionic polymerisation of isocyanates preferentially via the N=C bond,[241,248] in which it was shown, from quantum-chemical calculations, that at the instant of interaction with nucleophiles the N=C bond undergoes an intense polarisation (compared with the C=O bond), which explains its high reactivity in such processes.

The CT reaction of isocyanates was first considered as a special case of anionic homopolymerisation in two studies.[249,250] In the presence of typical catalysts of anionic polymerisation (sodium cyanide and others) at 173–253 K a linear polymer with a polyamide structure was obtained in a high yield (MW = 10^4–10^5) and the trimer was isolated as a side product. The authors proposed a general stepwise mechanism for the polymerisation of isocyanates under the influence of anions, in which the cyclotrimerisation reaction is a special case (Scheme 7):

Scheme 7



(1)

(2)

(3)

Pathway *a* responds to a low temperature and a low catalyst concentration and pathway *b* to a high temperature and a high catalyst concentration.

There is at present no doubt about the ionic character of the polymerisation of isocyanates.[60] Even under the influence of γ-radiation (^{60}Co) the process proceeds via a radical mechanism.[251] Cyclic trimers of aliphatic and aromatic isocyanates have been obtained by the anionic electroinitiated polymerisation.[252-254] The typical features of the cyclotrimerisation of isocyanates via the anionic mechanism are as follows. The activity of the isocyanates in cyclotrimerisation depends on the donor–acceptor properties of the substituents adjoining the NCO groups: isocyanates with electron-accepting substituents (aromatic) are more reactive than isocyanates with electron-donating substituents (aliphatic).[58,60,145] In a series of substituted phenyl isocyanates, those containing electron-accepting substituents in the *para*-position cyclotrimerise faster than the unsubstituted

PIC, while isocyanates with electron-donating substituents in the *para*-position cyclotrimerise more slowly.[60,95]

The high positive Hammett constant ρ for substituted isocyanates[59,95] shows that electron-accepting substituents increase k_{cat}, i.e. the activation process involves the electrophilic carbon centre of the isocyanate group. The initiation of the cyclotrimerisation of isocyanates as a result of the influence of nucleophilic groups on the electrophilic carbon atom of the isocyanate is also indicated by the increase of k_{cat} in the CT reaction with increase of the nucleophilicity of the catalytic centre, which has been recently demonstrated.[60,147,205]

It has been frequently noted in studies on the kinetics of the cyclotrimerisation of isocyanates in the presence of various kinds of catalysts at fairly low catalyst concentrations that the reactions investigated in many cases have an induction period, whose duration depends on the concentrations of the catalyst, the cocatalyst, the isocyanate, and the nature and polarity of the solvent. Inadequate attention has apparently been devoted to the study of the causes of the induction period in the cyclotrimerisation of isocyanates and of the relation between this factor and the overall process mechanism. Analysis of the data examined suggests that the appearance of the induction period in the cyclotrimerisation of isocyanates is due to the slow initiation, on the one hand, and the possibility of the action of an inhibitor, on the other.

It is known[150,255] that strong acids (for example, HCl) are effective inhibitors of the cyclotrimerisation of isocyanates at moderate temperatures. At the same time, the possibility of the presence of traces of HCl in isocyanates (which is almost always the case) is as a rule disregarded in kinetic studies. This may be the reason why a non-proportional dependence of the rate of cyclotrimerisation of the isocyanate on the catalyst concentration is sometimes observed at inhibitor concentrations comparable to those of the catalysts.[132] However, one should note that in the vast majority of experiments the reaction is of first order with respect to the catalyst.[60,62,74,94,118,125,128,136,137,144,150,168,172]

When the CT reaction of isocyanates is carried out in highly polar media (DMF, DMSO), an induction period is as a rule not observed, which indicates an increase of the rate of initiation in solvents of this kind. The study of the dependence of the rate of cyclotrimerisation of isocyanates on the dielectric constant of the medium[60] has demonstrated agreement with the Kirkwood equation.[256] This shows that the charge separation in the polymerisation active centre formed as a result of initiation is greater than in the initial reactants. On the other hand, it has been demonstrated that the rate of cyclotrimerisation of isocyanates cannot be unambiguously determined by properties of the solvents such as the dielectric constant and the dipole moment.[60,136] The electron-donating capacity of the solvent and the specific solvation of the reactants by the solvent also have a considerable influence under these conditions.[60,128,168]

The orders of the reaction of isocyanates observed in various experiments with respect to the main monomer ranged from zero[137] to two[60,147,150] and above,[155–158] depending on the type of catalyst used, the solvent, etc. In most cases the kinetic curves for the reaction obey a formal first-order kinetic equation.[62,74,94,136,150,168,172]

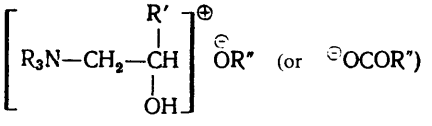
In non-polar and virtually non-solvating solvents (benzene, chlorobenzene), with the initiation as the slow stage limiting the rate of the main reaction, it has been noted that the order of the CT reaction of isocyanates with respect to the monomer is preferentially unity in terms of time and 2 in terms of concentration.[150,163,168] The above relations and also the finding that at the end of the induction period the reaction begins close to the maximum rate show apparently that initiation, involving the interaction of the catalyst with the isocyanate, leads to the formation of an initiator which is much more active than the highly polar initial catalyst.

In principle, when one considers the most effective catalysts of the cyclotrimerisation of isocyanates or the catalytic systems recommended at present for practical use, it is easy to see that they are all ion pairs with separated charges, in which the cation is to a considerable degree localised:

1. The alkali metal carboxylate (alkoxide)/oligoether systems consisting of solvate-separated ion pairs:[44,168]

$$M_s^{\oplus} \ldots {}^{\ominus}OCOR$$

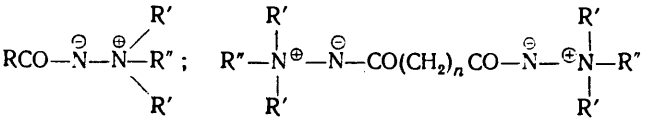
2. Quaternary ammonium derivatives obtained from tertiary amines, epoxyalkanes, and PD (water, alcohols, phenols, and carboxylic acids):[147,150,163,168,205]



(XIV)

Analysis of the structures of compounds of type (XIV) by means of quantum-chemical calculations[201,257] has shown that the anion in such compounds has a considerable capacity for free migration.

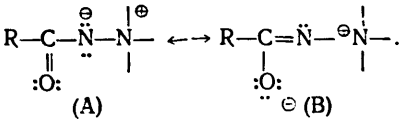
3. Aminoimides:[173–175]



(XV)

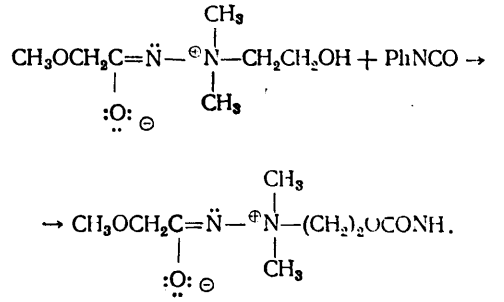
R, R′ = Alk; R″ = CH_2—CH(OH)—CH_3 or CH_2CH_2OH

The most active are the derivatives with primary OH groups. Acylamine imides are zwitter-ions having the following resonance structure:[173]

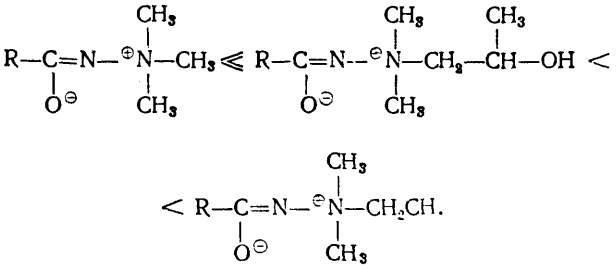


(A) (B)

From IR spectroscopic data, preference is given to structure (B). The authors have shown that the interaction of dimethyl-2-hydroxyethylaminomethoxyacetimide with PIC in acetonitrile leads to the formation of a carbamate:

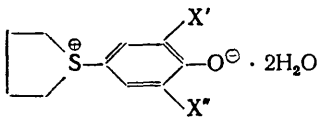


The authors believe that the carbamate promotes the induced polarisation of the isocyanate via the formation of a hydrogen bond and explain by its formation the higher catalytic activity of hydroxyl-containing acylaminoimides compared with the alkyl-substituted derivatives:



Unfortunately experimental kinetic data are not quoted in the relevant study,[173] which makes it impossible to infer the principal kinetic characteristics of the CT reaction of isocyanates in the presence of catalysts of this kind.

4. Sulphonium zwitter-ions:[159,160]



X', X'' = H, R

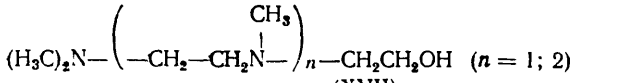
According to the data of Kresta et al.,[160] the CT reaction of PIC in acetonitrile in the presence of a catalyst of this kind is of first order with respect to the catalyst and of second order with respect to the monomer. At 298 K in the presence of this catalyst, a cyclic trimer is obtained in a quantitative yield; 93% of the trimer and 7% of a linear polymer are formed at 248 K and 64% of the trimer and 36% of the linear polymer are formed at 233 K. An important factor which determines the activity of the catalyst in the cyclotrimerisation of isocyanates is the nucleophilicity of the anion. With increase of the electron density of the oxygen atom in cyclic sulphonium zwitter-ions, the catalytic rate constant for cyclotrimerisation increases. Analogous results have been obtained by other workers[147] in the cyclotrimerisation of PIC in the presence of quaternary ammonium carboxylates as catalysts. At the same time, it has been shown[60] that the presence of bulky substituents in the anion of catalysts of the type of MOR does not exert a significant influence on the rate of cyclotrimerisation of PIC.

The characteristics noted above and others observed in the study of the kinetics of the cyclotrimerisation of isocyanates are the reason why there are at present no clear-cut ideas about the mechanism of this process despite the fairly large amount of experimental data. Generally speaking, all the hypotheses put forward concerning this question reduce to the consideration of two main process mechanisms: the insertion mechanism (or the mechanism of "insertion reactions) involving the M–X bond, where X = O, N, S,[61,155,203] or N–H,[84,87] and the mechanism involving addition to the anion.[41,86,94,136,168,258]

The template polymerisation mechanism has also been proposed for the cyclotrimerisation of isocyanates.[155–158]

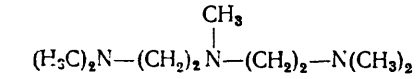
When ionic catalysts, which as a rule consist of ion pairs dissociated to different extents[128,147,168,205] or zwitter-ions,[159,160,173] are used for the cyclotrimerisation of isocyanates (which normally takes place at moderate or elevated temperatures), one should apparently consider polymerisation in the presence of separated ion pairs. In order to achieve the process involving free anions, the latter must be stabilised under these conditions.[41,215] The charge separation in the initial catalysts of the cyclotrimerisation of isocyanates of the type (XIII)–(XVI) is apparently a necessary but not a sufficient condition for effective catalysis via attack on the carbonyl component of the NCO group. Additional activation of the reactants is necessary, for example, the polarisation of the monomer and the catalyst by employing highly polar solvents or powerful solvating agents, which promotes the interaction of the catalyst with the isocyanate in the initiation stage.

In the study of the cyclotrimerisation of PIC in DMF in the presence of sodium ethoxide ($NaOC_2H_5$), it has been establisned[141–143] that in the presence of carbamates the rate of reaction increases in proportion to their concentration. The authors explained the cocatalytic effect of urethane by the polarisation of the NCO groups (as for hydroxyl-containing acylimides). The authors showed that, in the presence of carbamates the quantity ρ for the cyclotrimerisation of isocyanate diminishes under the conditions investigated. The authors suggest that the polarisation of the NCO groups then proceeds to an extent such that the inductive effect of the substituents in the aromatic ring of the isocyanate is less pronounced. However, the coordination interaction between the isocyanate and the urethane has not been observed.[259] The variation of the catalytic activity of hydroxyl-containing quaternary ammonium carboxylates in the catalysis of the cyclotrimerisation of isocyanates had also been attributed to the cocatalytic effect of the carbamate groups.[147,205] The recently observed catalytic activity of a series of tertiary amines having the structure



(XVII)

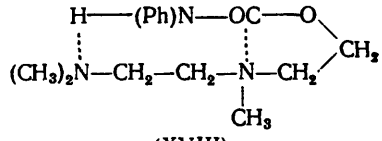
in the cyclotrimerisation of isocyanates has been explained by the same effect[172] on the basis of the fact that amines of the type



are ineffective under these conditions. However, it has been shown that dimethylethanolamine is also ineffective, like amines of the type

It has likewise been established that the cyclotrimerisation of isocyanates in the presence of catalysts of this kind in toluene is of first order with respect to the catalyst and the monomer and is characterised by the presence of an induction period, whose duration is inversely proportional to the catalyst concentration. Catalysts with primary OH groups are much more active than those with secondary hydroxyls; an increase of the number of substituents with OH groups at the same nitrogen atom returns the cyclotrimerisation of the isocyanate (analogously to the situation which obtains for quaternary ammonium carboxylates).[117] In the presence of an alcohol, the formation of a urethane in the presence of the catalysts indicated above always precedes the cyclotrimerisation and, under conditions where there is a slight excess of isocyanates (2 : 1), this is followed by the formation of the allophanate and cyclotrimerisation is observed only on further increase of the excess of isocyanate. The product of the addition of trimethylaminoethylethanolamine to PIC has been isolated and characterised[172] with the aid of infrared spectra and the following structure has been

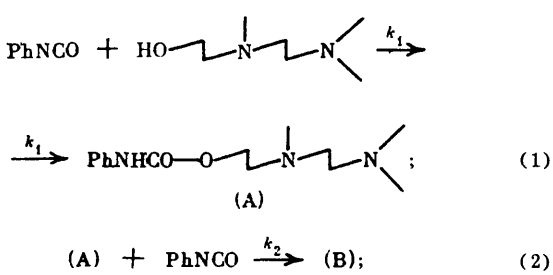
attributed to it:



(XVIII)

Since the urethane-formation reaction in the presence of catalysts of type (XVII) is of first order with respect to the alcohol and is almost independent of the isocyanate concentration, the authors believe that the complex (XVIII), formed rapidly in the presence of ROH, interacts with the alcohol, which entails the formation of a urethane and the regeneration of the catalyst. However, it is fairly difficult to imagine such interaction. It appears more probable that under these conditions the alcohol competes with the urethane in the complex formation reaction with the amine, forming the catalytic complex $R_3N.R'OH$ (in conformity with the general mechanism of the catalysis of the urethane-formation reaction by tertiary amines[260]), which then interacts comparatively rapidly with the isocyanate, forming the urethane. The trimerisation reaction is regarded as the consecutive addition of the isocyanate to the N–H bond in the complex (XVIII) (Scheme 8):

Scheme 8



(A)

$$(A) + PhNCO \xrightarrow{k_2} (B); \quad (2)$$

$$(B) + PhNCO \xrightarrow{k_3} (C); \quad (3)$$

$$(C) + PhNCO \xrightarrow{k_4} T + (A). \quad (4)$$

Bearing in mind that the product (A) is formed very rapidly, this scheme cannot, however, account for the induction period in the CT reaction with a subsequent high rate of the latter. In this connection, the authors, noting that the nature of the induction period is unknown, expressed the view, which conflicts with Scheme 8, that the induction period may be caused by the slow formation of a "synergistic intermediate complex". The possibility of the inhibition of the CT reaction by slowly reacting impurities is also allowed.

From the standpoint of a more complete explanation of the majority of the characteristics of the kinetics of the cyclotrimerisation of isocyanates in the presence of basic catalysts which have been observed and described here, the scheme proposed in a number of studies[60,163,168] is apparently more favourable. It can be represented in the following general form (taking into account the possible inhibition) (Scheme 9):

Scheme 9

$$A + I \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} X^* \text{ — initiation;} \quad (1)$$

$$\left.\begin{aligned} A + I &\xrightarrow{k_2} N, \\ X^* + I &\xrightarrow{k_2'} N', \end{aligned}\right\} \text{ inhibition;} \quad (2)$$

$$\left.\begin{aligned} X^* + I &\underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} XI^*, \\ XI^* + I &\underset{k_{-4}}{\overset{k_4}{\rightleftarrows}} XI_2^*, \end{aligned}\right\} \text{ chain propagation;} \quad (3)$$

$$XI_3^* + I \underset{k_{-5}}{\overset{k_5}{\rightleftarrows}} T + X^* \text{ — chain transfer;} \quad (4)$$

$$\left.\begin{aligned} XI_2^* &\xrightarrow{k_6} T + A, \\ XI_2^* + PD &\xrightarrow{k_7} T + A', \\ XI_2^* + Inh &\xrightarrow{k_8} T + N, \end{aligned}\right\} \text{ chain termination;} \quad (5)$$

Inh = inhibitor; N, N′ = inactive compounds.

Without taking into account the effect of the inhibitor and for conditions in a quasi-stationary process, where

$$k_1 > k_{-1};\ k_{-3} \ll k_3 \simeq k_4 \gg k_1;\ k_5 \gg k_6 \simeq k_7,$$
$$[A_0] = [A] + [X^*] + [XI^*] + [XI_2^*],$$

the above scheme can be described by the equations

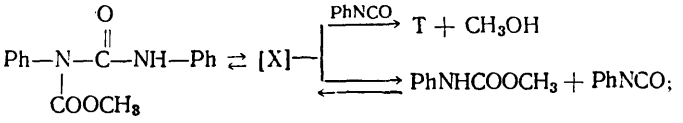
$$-\frac{d[I]}{d\tau} = k_{cat}\,\frac{[A_0][I]^2}{1 + B[I]};\quad B = \text{const};$$

$$\frac{[I_0] - [I]}{[I]\,[I_0]} + B \ln\frac{[I_0]}{[I]} = k_{cat}\,[A_0]\cdot\tau = k_{exp}\tau.$$

According to the results of Kresta and Hsieh,[60] the experimental results agree well with the latter equation. Scheme 9 includes, in principle, two kinetic chains: with regeneration of the initiator (X*) and with regeneration of the initial catalyst (A). Presumably the preferential realisation of one of them (depending on the reaction conditions and the type of catalyst) and the associated changes in the relative values of the constants for the individual stages of the process do in fact lead to differences between the observed characteristics of the CT reactions of isocyanates (different reaction orders with respect to the monomer, the presence or absence of the induction period, etc). When the rate of termination can increase during the reaction (for example, as a result of an increase in the concentration of active impurities and an increase of temperature), the reaction should be retarded according to the above scheme and there should be a corresponding increase of the reaction order with respect to the monomer (from first to second). Certain kinetic data indicate such features of the cyclotrimerisation of isocyanates.[147] However, the question of the structure of the initiator and of the interactions leading to its formation remains obscure.

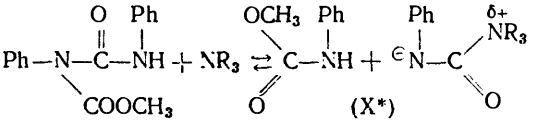
Examination of the kinetic data for the cyclotrimerisation of isocyanates reveals the striking fact that in many cases the reaction is accelerated in the presence of proton-donating compounds (alcohols, urethanes, and hydroxyl-containing catalysts),[84,141–143,147,172,173,205] even when highly basic catalysts are employed. In the presence of tertiary amines (TEDA) at moderate temperatures the cyclotrimerisation of isocyanates takes place only in the presence of an alcohol, urethane, or allophanate in the system.[137,171] Another feature which has been observed by some investigators consists of facts indicating that the reaction preceding cyclotrimerisation[84,172] or coupled with it[137,171] involves the formation-dissociation of the allophanate.

In the presence of 2-methyltriethylenediamine the cyclotrimerisation of PIC in chlorobenzene was not observed at 353 K for 2–3 h;[137,171] when methyl αγ-diphenylallophanate (MDA) was introduced into this system, PIC trimerised at a high rate. It has also been shown that in the presence of 2-methyltriethylenediamine and MDA the cyclotrimerisation of PIC begins with an induction period, the duration of which is inversely proportional to the MDA concentration and depends only slightly on the isocyanate concentration. The rate of the main reaction under these conditions is proportional to the concentrations of the catalyst and MDA and is independent of the concentration of the monomer. It was established that two coupled reactions take place in the system: the dissociation of the allophanate and cyclotrimerisation with a common induction period, whose nature the authors explain by the influence of the inhibitor on the intermediate (X) formed from the allophanate:



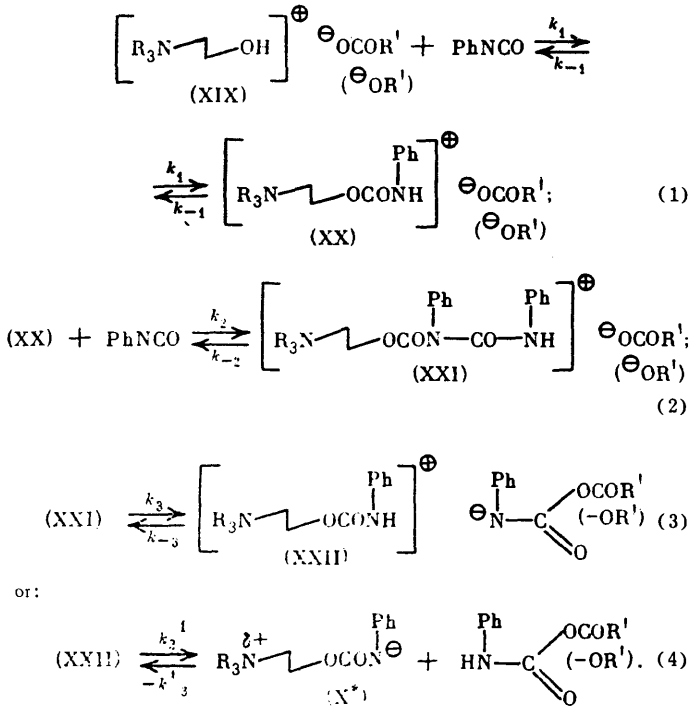
The action of the inhibitor precisely on the product (X) is caused, in their view, by the fact that the induction period persists even in the presence of a high content of MDA, which is known to exceed the possible content of the inhibitor.

On the other hand, one can assume that the formation of active polymerisation centres (X*) in systems of this kind is coupled with the allophanate dissociation step via the interaction of the catalyst with its active (possibly tautomeric) form:



Since this stage is apparently extremely slow (bearing in mind the reversibility of the process) and limits the rate of cyclotrimerisation of the isocyanate, the latter is almost independent of the isocyanate concentration but should be proportional to the MDA and catalyst concentrations. On the other hand, the possibility that the inhibitor acts on the active centres just as much as the initial catalyst cannot be ruled out in this case either. The appearance of active polymerisation centres of the type (X*) can lead to the cyclotrimerisation of isocyanates at a higher rate than that observed at the end of the induction period of the reaction. From the standpoint of the possible involvement of the allophanate in the initiation step of the cyclotrimerisation of isocyanates (via the interaction of its active form with the catalyst), it is apparently possible to explain also other instances of the influence of hydroxyl-containing agents (or urethanes) on the kinetics of this reaction; presumably in the presence of hydroxyl-containing quaternary ammonium carboxylates (alkoxides) the following interactions take place in the initiation process (Scheme 10):

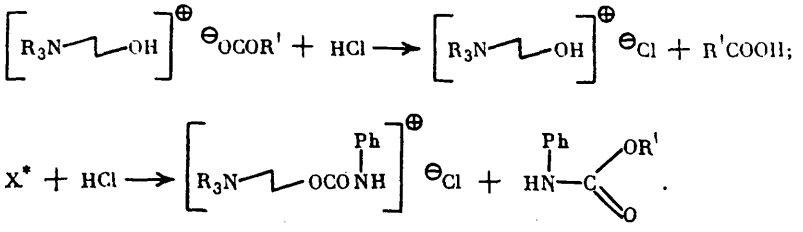
Scheme 10



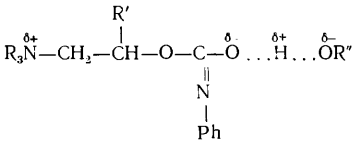
Stages (2) and (3) can then involve additional interactions.

The separated ion pair (XXII), which is more polar than the initial catalyst, or the dipolar anion (X*) initiates the CT process at a high rate in conformity with stages (3) and (4) (Scheme 9). Chain termination may be caused under these conditions by the regeneration of products of the type (XIX) or (XX) in the cyclisation stage and also by the inhibition of the active centres by impurities. With increase of temperature, the probability of such termination also increases, which may lower the rate of cyclotrimerisation of isocyanates.[132] The shift of equilibrium in stages (2) and (3) (Scheme 10) to the left should also diminish the rate of the main process.

In terms of Scheme 10, it is possible to explain also the decrease of the activity of catalysts of this kind when the primary hydroxy-groups are replaced by secondary hydroxy-groups and following an increase of the number of OH-containing substituents. The addition of carboxylic acids to such systems should entail the formation of associated species with the anion[261] and hence a decrease of the activity of the catalyst. Strong acids (HCl) can apparently convert into an inactive form both the initial catalyst and products of type (X*), inhibiting thereby the cyclotrimerisation of the isocyanate:



Analogously, it is possible to account for the catalytic activity in the cyclotrimerisation of isocyanates of a number of hydroxyl-containing amines[172] and acylaminoimides,[173] as well as the activity of carbamates as cocatalysts in the cyclotrimerisation of isocyanates in the presence of C_2H_5ONa.[141-143] The possibility of the dissociation of a urethane in the presence of products of type (III), which has been established recently,[8] also constitutes a precondition for the formation of initiators of type (X*) in systems containing a urethane (allophanate) and a strong base. One cannot rule out the possibility that products of this kind are formed also in reactions involving the possible interaction of the isocyanate trimer with an epoxide in the presence of catalysts (strong bases) or with the product of the addition of the epoxide to the catalyst of type (III)–(V), and ultimately lead to the formation of oxazolidinones[202] or products having the tentative structure[262]



The study of the above characteristics of the kinetics and the proposed mechanism of the CT reaction of isocyanates from the standpoint of conformational ideas[263] is undoubtedly of great interest.

The data presented in this review indicate the great variety of catalysts and catalytic systems used in the cyclotrimerisation of isocyanates and also the existence of different points of view on the mechanism of this reaction. Analysis of the data available on this question established that the most effective catalysts of the cyclotrimerisation of isocyanates are ion pairs with separated charges in which the active centre is the anion, the counterion being fairly well localised.

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The Reactivity of 1,3,2-Diheterophosphacyclanes Containing a Pentacoordinate Phosphorus Atom

N.A.Polezhaeva and R.A.Cherkasov

Studies on the reactivity of λ^5-1,3,2-diheterophosphacyclanes obtained during the last ten years are examined and described systematically. Data concerning new prototropic and elementotropic processes involving derivatives of pentacoordinate phosphorus are presented. Attention has been concentrated on the elucidation of the influence of the incorporation of a phosphorus(V) atom in the ring on the reactivity of phosphoranes in reactions of various types. The role of phosphorus(V) compounds as intermediates in reactions of phosphorus compounds involving different types of coordination of the phosphorus atom is demonstrated.
The bibliography includes 176 references.

CONTENTS

I.	Introduction	1126
II.	Hydrophosphoranes	1126
III.	Hydroxyphosphoranes. The phosphate-phosphorane tautomerism	1130
IV.	Aminophosphoranes. The phosphimide-phosphorane tautomerism	1137
V.	Other tautomeric transformations of phosphoranes. Phosphorotropic processes	1139
VI.	Thermolysis of phosphoranes	1140
VII.	Nucleophilic substitution at a pentacoordinate phosphorus atom	1142

I. INTRODUCTION

The study of the relation between the structure and reactivity of 1,3,2-diheterophosphacyclanes containing tricoordinate[1] and tetracoordinate[2] phosphorus atoms revealed the specific features of the chemical behaviour of these organophosphorus compounds (OPC) associated with the inclusion of a phosphorus atom in the cyclic molecular skeleton. The reactivity of five-membered cyclic OPC of the above type has been found to be particularly unusual, which was manifested in the kinetic, synthetic, and stereochemical results of the reactions involving them.

In the present review an attempt is made to give a systematic account of the survey of the literature data on the reactivity of heterocyclic compounds of pentacoordinate phosphorus containing in the cyclic fragment, together with the phosphorus(V) atom, two other identical or different heteroatoms (O, N, S), namely λ^5-1,3,2-diheterophosphacyclanes. In a number of instances data on the reactivities of acyclic phosphorus(V) compounds and 1,2-heterophosphacyclanes with a similar ligand environment around the phosphorus atom are adduced for comparison.

In the review literature available hitherto attention has been concentrated on the structural[3-5] and to a lesser extent the synthetic[6-8] chemistry of compounds of pentacoordinate phosphorus. Although modern ideas about the structure, the ligand reorganisation processes, and the role of intermediates of the phosphorane type in the chemical reactions of OPC have been developed precisely in relation to λ^5-1,3,2-diheterophosphacyclanes,[9] the relation between the structure and reactivity of these OPC has been studied systematically only for a few examples.[10] During 1970–1980, new experimental data were obtained which deepened our knowledge about the chemical behaviour of compounds of pentacoordinate phosphorus. New types of phosphoranes were synthesised; some of them are stable models of the intermediates formed in reactions of compounds with different types of coordination of the phosphorus atom. New types of prototropic and elementotropic tautomeric systems, including phosphorotropic systems, containing the phosphorus(V) atom have been discovered. Data concerning the mechanisms of nucleophilic substitution reactions at a pentacoordinate phosphorus atom have been obtained for the first time. New possibilities for the employment of phosphorus(V) compounds in organic synthesis have been demonstrated.[11] The "hydroxyphosphorane concept", which is a compilation of empirical rules governing the structure and character of the ligand and valence isomerisation of the phosphorane molecules, has been developed further.[12]

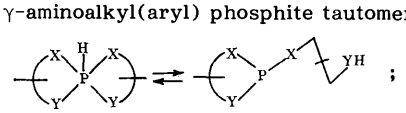
These and other results of the studies during the last ten years are included in the present review. The synthetic and stereochemical aspects of the chemistry of λ^5-1,3,2-diheterophosphacyclanes are used only to the extent that they are necessary for the elucidation of the characteristics of the reactivity of OPC of this type.

II. HYDROPHOSPHORANES

Information about the methods of synthesis and the chemical properties of hydrophosphoranes obtained in the early stages of the development of the chemistry of these compounds of pentacoordinate phosphorus, containing a P–H bond, are presented in the relevant reviews[13-15] and are not included in the present review. The principal characteristic features of the tautomeric processes involving such compounds and the results of the study of their reactivity obtained during recent years are considered here.

1. The Phosphate–Phosphorane Tautomerism

The isolation of the first spirophosphoranes and somewhat later of monocyclic phosphoranes with a P–H fragment (see Pudovik et al.[1] and Arbuzov and Polezhaeva[10] and the literature quoted therein) made it possible to establish the existence of the hydrophosphorane–γ-hydroxyalkyl(aryl) phosphite or γ-aminoalkyl(aryl) phosphite tautomeric equilibrium:



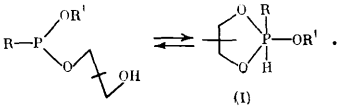
X, Y = NR, O .

The position of this equilibrium depends on the structure of the compound, the medium, and temperature. The phosphorane form is more characteristic of spirocyclanes substituted at the carbon atoms, those containing a secondary amino-group, and unsaturated and aromatic systems. A decrease of temperature promotes an increase of the content of the phosphorus(V) isomer. The introduction of substituents at the endocyclic nitrogen atom in λ^5-oxazaphospholans shifts the equilibrium towards the phosphite.[10,16]

The ease of the phosphorus(V) → phosphorus(III) transition is determined to a large extent by the nature of the endocyclic heteroatoms. For X = Y = O, the equilibrium is displaced towards the spirophosphorane even at room temperature, particularly in the case of substituted rings.[17] For asymmetrically substituted rings, two and sometimes three phosphorus(III) forms can exist in equilibrium with the hydrophosphorane.

Although a correlation between the polarity of the solvent and the content of the phosphite form at equilibrium has not been observed, it has been established that basic solvents shift the equilibrium towards phosphorus(III), while acid solvents shift it towards phosphorus(V).

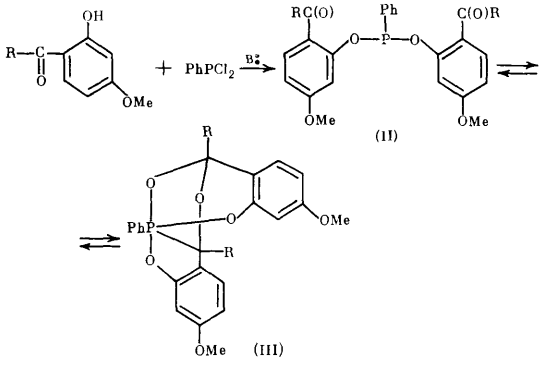
An analogous equilibrium for monocyclic phosphoranes has been detected by ^{31}P NMR; in this case too a decrease of temperature favours the formation of the phosphorus(V) form:



(I)

Hydrophosphoranes of type (I) are interesting because they are intermediates in many reactions of derivatives of tervalent phosphorus with proton-donating reagents (see Pudovik et al.[1] and the literature quoted therein) and also serve as the starting compounds for the synthesis of alkylspirophosphoranes with a P–R bond.[18]

The type of tautomerism described is characteristic mainly of hydrophosphoranes, but the observation of the phosphite–phosphorane tautomerism in the phenylphosphonite (II)–polycyclic phenylphosphorane (III) system has been reported:[19]



(II)

(III)

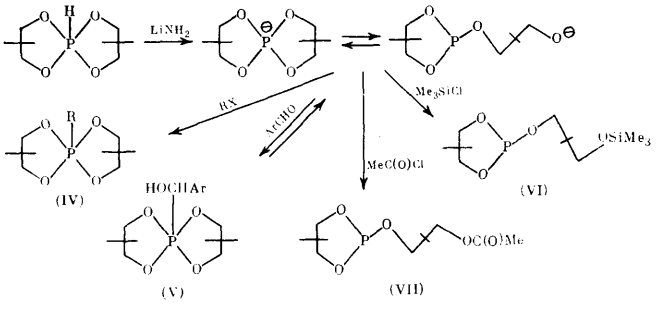
When the polycyclic phosphorane (III) is dissolved in $CHCl_3$, the equilibrium is established in 1 h at 25 °C.

The reactivity of hydrophosphoranes is determined mainly by the phosphite–phosphorane equilibrium and the presence of a fairly mobile P–H proton in the phosphorane isomer. The electrophilic properties of the pentacoordinate phosphorus atom, which predetermine the behaviour of spirophosphoranes and in general of phosphorus(V) derivatives as Lewis acids, play a significant role. In the phosphorus(III) form the reactions can involve one of two nucleophilic centres—the tricoordinate phosphorus atom and the YH(XH) group.

Estimation of the acid properties of hydrophosphoranes[20] demonstrated a decrease of the H-donating capacity following the replacement of endocyclic oxygen atoms by the NH group [apparently as a consequence of the greater $(p-d)_\pi$ donor capacity of the nitrogen atom compared with oxygen[20]] and on transition from spirocyclic to monocyclic hydrophosphoranes. The reactivity of hydrophosphoranes in the reaction with diphenyldiazomethane increases in parallel with the enhancement of the acid properties.[20]

The ease of the abstraction of the P–H proton on treatment of hydrophosphoranes with various metallating agents (metal hydrides and amides and organometallic compounds) is also determined by the structure of the phosphorane.[21,22] Whereas a proton can be abstracted from hydrophosphoranes which are derivatives of pinacol by metal amides (but not hydrides), hydrophosphoranes containing an endocyclic or exocyclic carbonyl group are deprotonated even by diethylamine

According to ^{31}P NMR data, the metallic derivatives of hydrophosphoranes are O anions and not P anions (the $^1J_{PH}$ doublet disappears and the signal of tricoordinate phosphorus appears).[21] However, a dual reactivity is characteristic of these compounds. Their alkylation by alkyl halides, alkenyl halides, and alkyl sulphates gives rise to a product with a spiran structure (IV). In the reactions with aromatic aldehydes the products are α-hydroxyalkylspirophosphoranes (V) which are thermally unstable and on heating regenerate the initial spirophosphorane and the aldehyde. The phosphoranes (V) can be formed also without the participation of metals (see below). Silylation and acylation involve the terminal oxygen atom of the phosphite group and lead to the phosphites (VI) and (VII) respectively.[21] We may note that the reactions of the hydrophosphoranes themselves with acyl chlorides in the presence of tertiary amines also lead to γ-acetoxyalkyl phosphites (VII),[23] while acylation of λ^5-oxazaspirophospholans by acetic anhydride ruptures both P–N bonds:[24]



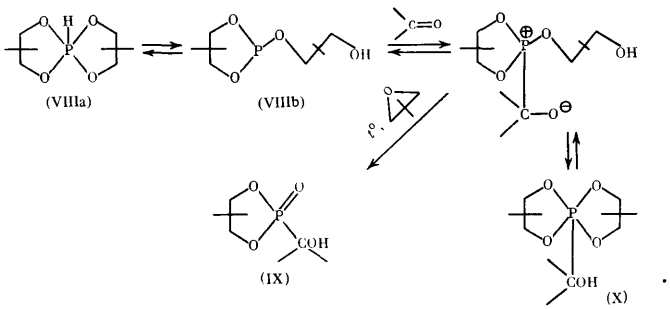
(IV) (V) (VI) (VII)

An analogy with dialkyl phosphites is manifested in these reactions: metallation takes place at the oxygen atom and the subsequent reactions with electrophiles can proceed via both the oxygen and phosphorus atoms.

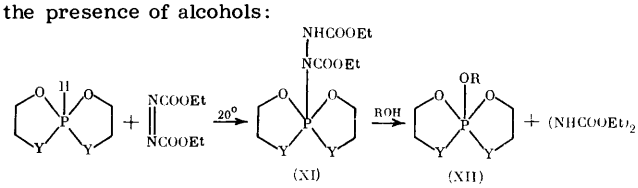
Like dialkylphosphorous acids, hydrophosphoranes interact with aliphatic aldehydes,[21,25] activated ketones, and animals[23,26] and add to electrophilic unsaturated systems.[27,28]

As already stated, although the α-hydroxyalkylspirophosphoranes formed on addition of hydrospirophosphoranes to aldehydes can be isolated, they are unstable and readily decompose. It has been suggested[26] that these reactions involve the nucleophilic addition of the phosphorus(III) atom of the form (VIIIb) to the carbon atoms of the carbonyl group; the dipolar ion, whose formation is promoted by an excess of the carbonyl reagent, is stabilised in two ways:

the elimination of the epoxide leads to cyclic α-hydroxyphosphonates (IX), while cyclisation gives rise to spirophosphoranes (X):



Imines are less reactive in the addition reactions of hydrospirophosphoranes than the aldehydes with a similar structure;[28] in the presence of alcohols cyclic enamines oxidise hydrospirophosphoranes to the corresponding pentaoxaspirophosphoranes.[29] The oxidation products (XII) are obtained ultimately also on interaction with azodicarboxylic ester in the presence of alcohols:

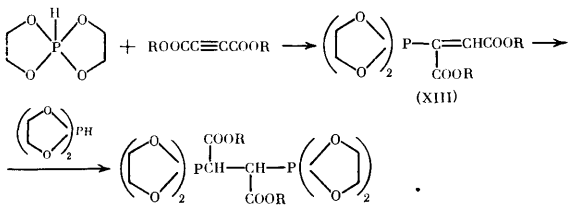


It has been suggested[30] that the adduct (XI) is formed initially, but it is unstable and has not been isolated.

The reactions of hydrospirophosphoranes with aldehydes, ketones, and imines are reversible and their thermodynamically controlled products are phosphoranes with an exocyclic P–C bond. Like the interaction with phenyl azide[31] and with certain other unsaturated systems,[23,25,28,29] these reactions are characteristic only of the hydrophosphoranes which are in equilibrium with the phosphite form; in the absence of the latter, there is no reaction.

In the general case the reactivity of λ^5-1,3,2-diheterophospholans with P–H bonds in reactions with electrophiles depends to a large extent on the nature of the heteroatoms attached to the phosphorus atom. Spirophosphoranes containing even one 1,3,2-oxazaphospholan ring are more reactive than tetrahydroxyspirophosphoranes.[28]

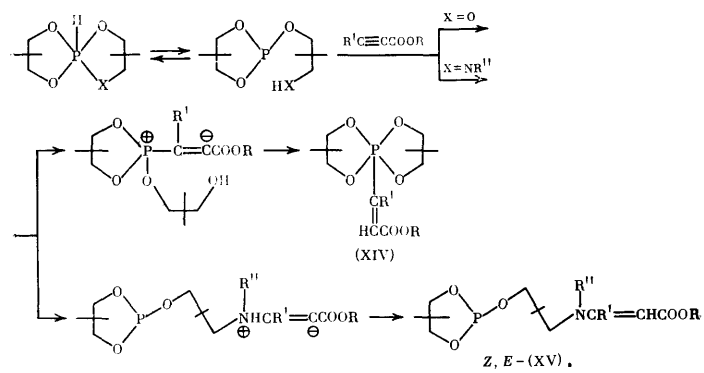
The nature of the endocyclic heteroatom of hydrospirophosphoranes influences also the synthetic result of the reactions involving addition to acetylenic reagents. Tetrahydroxyhydrophosphoranes readily add to acetylenedicarboxylate esters and proprionates with formation of vinylphosphoranes (XIII).[32] The adduct (XIII), which exists in the form of two stereoisomers, which can be separated by crystallisation, combines with a second molecule of hydrophosphorane at an elevated temperature:



It is striking that the P–C bond in the vinylphosphorane is fairly labile and is readily broken on treatment with an alcoholic solution of sodium alkoxide.[33] This can be accounted for by the high electrophilicity of the phosphorus-(V) centre.

If the spirophosphorane contains even one endocyclic P–N bond, then the reaction products are the stereoisomeric phosphites (XV). However, ring-substituted λ^5-oxazaphospholans and λ^5-dioxaphospholans form compounds of pentacoordinate phosphorus of type (XIV). It has been suggested[34] that the phosphite formed is involved in the addition process (Scheme 1); hydrophosphoranes which are not in equilibrium with the phosphorus(III) isomer are inert in such reactions.

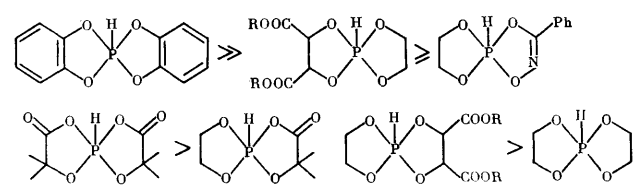
Scheme 1



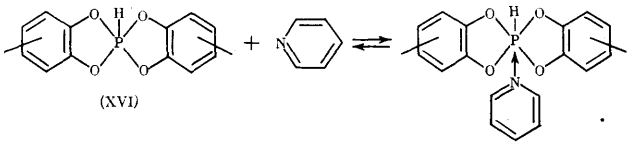
The mechanism presented in Scheme 1 is supported by the fact that alcohols do not react with these acetylenic compounds, whereas secondary amines readily add to them. The interaction of the γ-aminoalkyl cyclic phosphite isomer therefore involves the terminal amino-group like the addition of amines, while the oxa-analogues add as a result of the nucleophilic attack by the tervalent phosphorus atom on the β-carbon atom of the acetylenic group.[32–34]

Vinylphosphoranes of types (XIII) and (XIV) combine with a second hydrospirophosphorane molecule slowly, while the addition of dialkyl phosphites (in the presence of bases) is rapid. This difference has been attributed[33] to the different nucleophilic properties and steric hindrance of the phosphorus centres of the addends. In the addition of vinylphosphoranes, the nucleophile is subjected to a β-directing effect [in relation to phosphorus(V)], as in the analogous reactions of the vinyl derivatives of tricoordinate and tetracoordinate phosphorus. Only the vinylphosphorane obtained from propiolic acid esters (XIV, R' = H) combines with amines at the α-carbon atom.[33] Presumably the β-directing effect under conditions involving competition between the electron-accepting substituents in compound (XIV) is more pronounced for the alkoxycarbonyl group than for the spirophosphoranyl group.

Numerous data demonstrating the manifestation of the Lewis acidity of the phosphorus atom in hydrophosphoranes have been obtained. The following series, based on the weakening of this acidity, which agrees with the decrease of the overall electron-accepting capacity of the substituents in λ^5-diheterophospholan rings, have been found:[22]



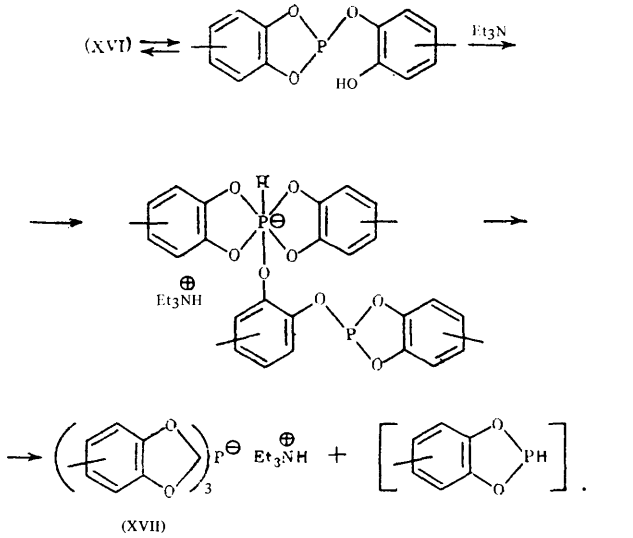
The Lewis acidity of hydrophosphoranes predetermines their capacity for coordination to bases, which increases the coordination number of the phosphorus atom to six:[35]



(XVI)

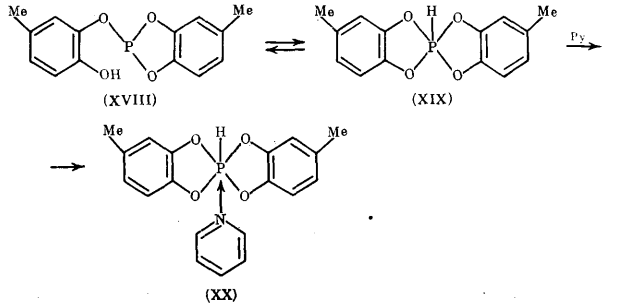
According to ^{31}P NMR data, the reversible reaction of compound (XVI) with pyridine leads to compounds of hexacoordinate phosphorus, whose content in the equilibrium mixture increases with increase of temperature. An analogous phenomenon obtains also when other spirophosphoranes without the P–H fragments are used, but in these cases it is less marked.[36]

The interaction of substituted dibenzohydrospirophosphoranes (XVI) with bases stronger than pyridine (triethylamine, triethylenediamine, and diisopropylamine) leads to the phosphoranes (XVII) as a result of the interaction of the two tautomeric forms of the hydrophosphorane:[37]



(XVII)

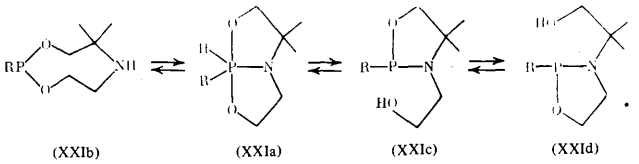
The above data indicate the ability of hydrophosphoranes to be involved in a tautomeric equilibrium with γ-hydroxyalkyl(aryl) phosphites, on the one hand, and (in basic media) with derivatives of hexacoordinate phosphorus, on the other. The presence of both types of equilibria has been established in the (XVIII) ⇌ (XIX) ⇌ (XX) system:[36]



(XVIII) (XIX) (XX)

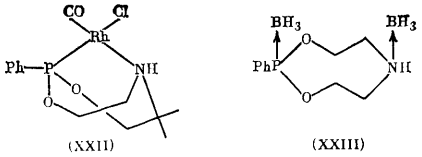
With increase of the amount of pyridine, the equilibrium shifts towards the "phosphorate" (XX).

Tautomerism involving the formation of the forms (XXI, b–d) is potentially possible for the bicyclic hydrophosphoranes (XXIa):



(XXIb) (XXIa) (XXIc) (XXId)

Only the phosphorane (XXIa), which has been found to be involved in the P–H P–D deuterium exchange, has been detected in solution;[38–40] the form containing a phosphorus-(III) atom has been identified in the gas phase by photoelectron spectroscopy.[41] Bicyclohydrophosphoranes combine with phenyl azide.[42] They react with transition metals to form complexes in which the coordinated ligand can exist in a monodentate or bidentate monocyclic phosphite form of type (XXII).[43–46]

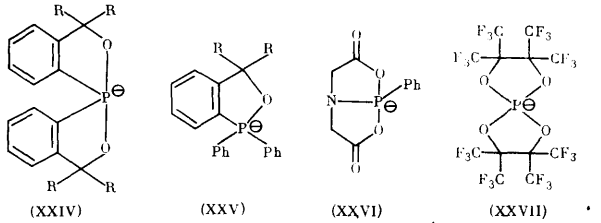


(XXII) (XXIII)

The adduct (XXIII), containing two molecules of the complex-forming agent, has been obtained by the interaction of (XXIa, R = Ph) with $Me_2S.BH_3$.[42]

2. Phosphoranide Anions

As pointed out above, the deprotonation of hydroxyspirophosphoranes results in the formation of phosphoranide anions, which may be involved in a tautomeric equilibrium with phosphite-alkoxides.[47,48] This method of generating stable cyclic phosphoranide anions has been used[48–52] for the synthesis of stable cyclic anionic systems (XXIV)–(XXVII) from the corresponding hydrophosphoranes; the bases employed were butyl-lithium[50,51] or triethylamine:[48,52]

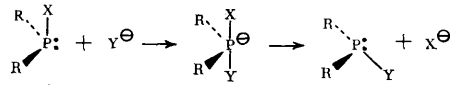


(XXIV) (XXV) (XXVI) (XXVII)

R = Me, CF_3

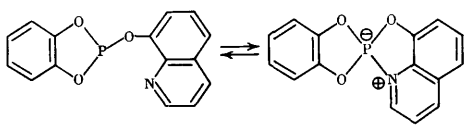
X-Ray diffraction (XRD) data for the anion (XXVII) have shown that it has the structure of a distorted trigonal bipyramid (TBP) with the unshared electron pair (LEP) in the equatorial (*e*) position and with a large difference between the lengths of the axial (*a*) P–O bonds (1.77 and 2.02 Å).[48]

Species of the type of phosphoranide anions have been postulated as unstable intermediates in bimolecular nucleophilic substitution reactions at a tricoordinate phosphorus atom:[1,53]



The isolation and identification of stable phosphoranide anions is of fundamental importance for the understanding of the mechanisms of nucleophilic substitution at the atoms of not only tricoordinate[1] but also tetracoordinate[2] and pentacoordinate (see Section VII) phosphorus atoms, which, at least in cyclic OPC, can proceed via a stage involving the formation of intermediates with an increased, compared with the initial phosphorus compound, coordination number of the central atom.

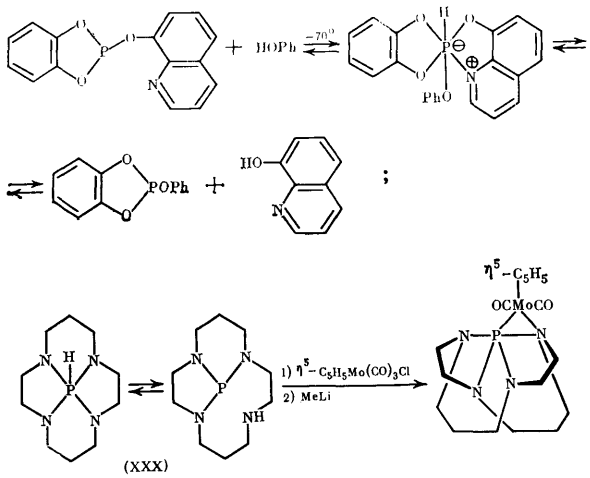
A phosphoranide centre can be formed also intramolecularly:[54]



(XXVIII) (XXIX)

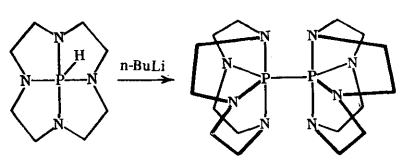
The equilibrium (XXVIII) ⇌ (XXIX), detected by ^{31}P NMR, is strongly displaced towards the form (XXVIII). Intermolecular nucleophilic substitution in this system takes place via an intermediate with a hexacoordinate phosphorus atom.[55]

Unusual polycyclic phosphoranides have been synthesised by the reaction of the hydrophosphorane (XXX) with transition metal compounds.[56] According to XRD data, the phosphorus ligand in these compounds is bidentate and is coordinated to the metal atom via both the phosphoranide and amine centres.

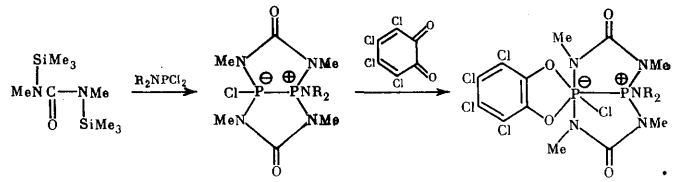


(XXX)

We may note, incidentially, that the first diphosphorane compound with a P(V)–P(V) bond has been obtained from a polycyclic hydrophosphorane:[57]



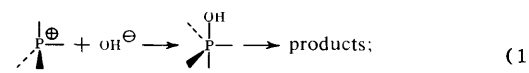
Compound (XXXI) contains a direct bond between the phosphonium and phosphoranide phosphorus atoms. The interaction with chloranil results in the formation of a "phosphoniaphosphorate"—the first compound with a P(IV)–P(VI) bond:[58]



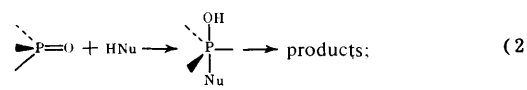
(XXXI)

III. HYDROXYPHOSPHORANES. THE PHOSPHATE–PHOSPHORANE TAUTOMERISM

The development of the chemistry of hydroxyphosphoranes is closely related to modern ideas concerning the mechanism of nucleophilic substitution reactions at a tetrahedral phosphorus atom [$S_N2P(IV)$], which are based on the rules associated with the hydroxyphosphorane concept—intermediates having a TBP structure with a pentacoordinate phosphorus atom are formed in these processes (see Cherkasov et al.[2] and the literature quoted therein). The character of such intermediates determines to a large extent the reactivity of phosphorus(IV) compounds and the synthetic and stereochemical results of nucleophilic substitution reactions. On hydrolysis of phosphonium salts [Eqn.(1)] or solvolysis of phosphoryl compounds by proton-containing nucleophiles [Eqn.(2)], the above TBP intermediates should have the hydroxyphosphorane structure:



(1)



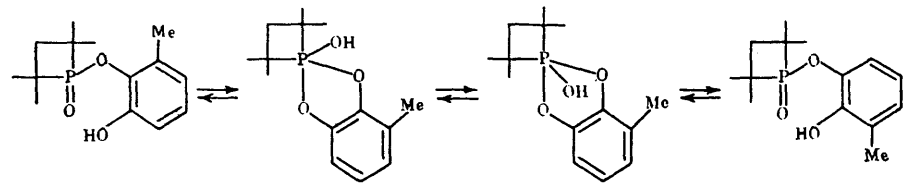
(2)

Nu = nucleophile.

The identification of the hydroxyphosphoranes and the study of their properties are therefore of decisive importance for the demonstration of a two-stage mechanism of the nucleophilic substitution reactions at phosphorus(IV), including biochemical phosphate transfer processes.[2,59,60]

Nevertheless, until the end of the 1970's, the demonstration of the formation of hydroxyphosphoranes in the nucleophilic reactions of phosphorus(IV) remained an unsolved problem. The first unambiguous evidence for the formation of hydroxyphosphoranes was obtained in the study of the interaction of cyclic phosphoryl compounds with proton-containing nucleophiles[2] and the hydroxyphosphoranes were trapped directly and successfully characterised in a study of the isomerisation of γ-hydroxyalkyl(aryl) esters of cyclic quinquevalent phosphorus acids (see Cherkasov et al. and the literature quoted therein[2]). Methods for the synthesis of stable hydroxyphosphoranes were subsequent developed.

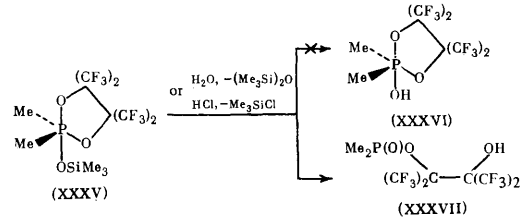
The 5-hydroxy-2-methylphenyl ester of the cyclic four-membered phosphinic acid (XXXII) shows signs in solution of a dynamic equilibrium due to the isomerisation (XXXII) ⇌ (XXXIV) involving the intermediate formation of the hydroxyphosphoranes (XXXIII, a and b):[61]



(XXXII) (XXXIIIa) (XXXIIIb) (XXXIV)

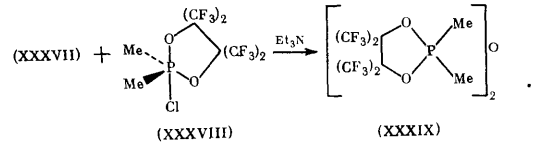
The activation energy for the isomerisation process is 17 kcal mol^{-1}. The concentration of compounds (XXXIII) is insufficient for their direct detection by NMR, but the possibility of their formation has been demonstrated by the reaction of a mixture of compounds (XXXII) and (XXXIV) with diazomethane: the methyl ester of the acid (XXXIII) was obtained in 5% yield. It is striking that the activation barrier to the isomerisation of the acyclic analogues (XXXII) is 24 kcal mol^{-1} for diphenylphosphinate and 28.3 kcal mol^{-1} for diphenylphosphinothioate, which reflects the well known sequence in the decrease of the energy of the TBP on passing from acyclic to monocyclic and spirocyclic structures[2] and the lower stability of mercaptophosphoranes compared with hydroxyphosphoranes.[62]

In this connection we may also note that, when the monocyclic siloxyphosphorane (XXXV) is acidified or cautiously hydrolysed, the product is not the hydroxyphosphorane (XXXVI) but the isomeric γ-hydroxyalkyl phosphinate (XXXVII):[63]



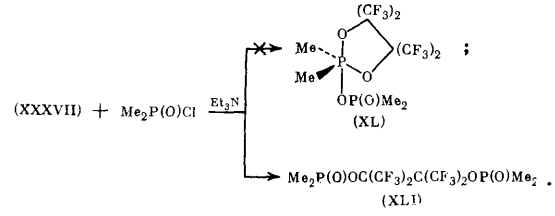
(XXXV) (XXXVI) (XXXVII)

However, it is of interest that the reaction of the phosphinate (XXXVII) with the chlorophosphorane (XXXVIII) proceeds with transfer of the reaction centre and leads to the anhydride of the hypothetical P(V)–OH acid (XXXIX):



(XXXVII) (XXXVIII) (XXXIX)

However, the acyclic chloride of dimethylphosphinic acid converts compound (XXXVII) into the symmetrical bisphosphinate (XLI) and not into the mixed anhydride (XL):[63]

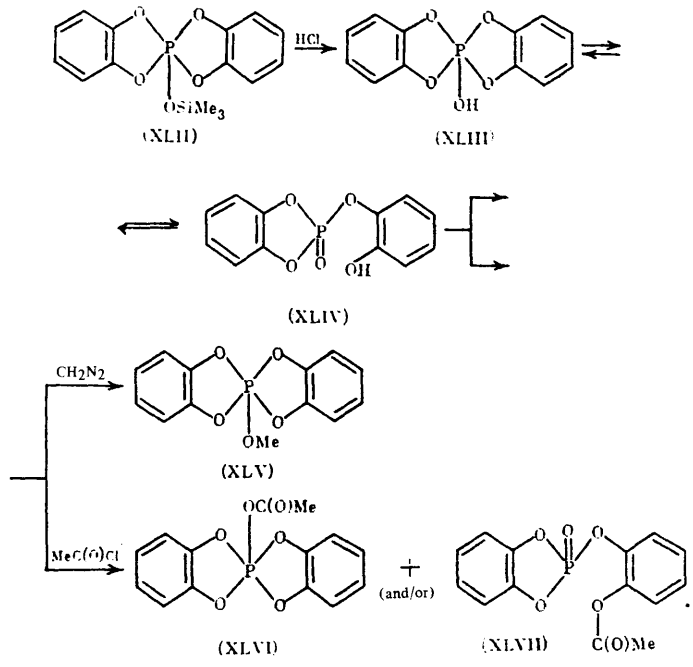


(XL) (XLI)

The formation of hydroxyphosphoranes has been postulated also in other reactions of γ-hydroxyalkyl(aryl) esters of phosphorus(IV) acids.[2]

These results indicate the possibility of the existence of a fairly mobile phosphate–phosphorane equilibrium involving hydroxyphosphoranes, which has been demonstrated for the first time by Ramirez et al.[64] and by Chang Bui Cong et al.[65] The product of the desilylation of bis(phenylenedioxy)siloxyphosphorane (XLII) has the structure of the phosphate (XLIV) in the crystalline state[66] [cf. the hydrolysis of the siloxyphosphorane (XXXV) to the phosphinate (XXXVII) [63]]. However, in acetonitrile at −48 °C the ^{31}P NMR spectrum showed two signals due to the phosphorus nucleus: the hydroxyphosphorane (XLIII) [$\delta(^{31}P) = 27.0$] was found together with the phosphate (XLIV) [$\delta(^{31}P) = +6.7$] in equilibrium with the latter and its amount was greater than that of the phosphate—the ratio P(IV) : P(V) = 1 : 1.5. The content of the phosphorus(V) form increases in the more basic acetone (3 : 1 at −48 °C):

Scheme 2



(XLII) (XLIII) (XLIV) (XLV) (XLVI) (XLVII)

Treatment of the (XLIII) ⇌ (XLIV) mixture with diazomethane affords a qualitative yield of the methoxyphosphorane (XLV); acetylation leads to a mixture of the acetyl derivatives of the phosphorane (XLVI) (20%) and the phosphate (XLVII) (80%) (Scheme 2). However, one should note that the synthetic result of the acetylation of compound (XXXV) or the (XLIII) ⇌ (XLIV) mixtures does not reflect the contents of the phosphorus(IV) and phosphorus(V) forms in the solutions: the reactions can proceed with transfer of the reaction centre [this has been confirmed

particularly strikingly by the reaction (XXXVII) + (XXXVIII) → (XXXIX) or may be subject to thermodynamic control. It has been established that the acetoxyphosphorane (XLVI) can be partly isomerised to the phosphate (XLVII) under the influence of the HCl evolved in the reaction.[66]

In the general case an increase in the content of the phosphorus(V) form in the hydroxyphosphorane–phosphate equilibrium is promoted by a decrease of temperature, by an increase of the basicity of the medium, and by the enhancement of the electron-accepting properties of the dioxyalkylene(arylene) substituent.

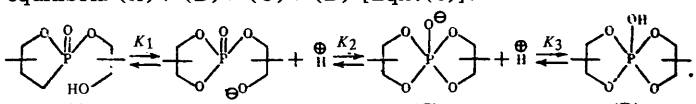
The intensity of the hydroxyphosphorane signal in the ^{31}P NMR spectra of the P(V) ⇌ P(IV) mixture begins to increase with decrease of temperature in those cases where individual lines correspond to each of the two forms P(V) and P(IV) [slow, in terms of the NMR time scale, equilibria of the type (XLIII) ⇌ (XLIV) and (LVI) ⇌ (LVIa) (Table 1)]. The averaged signal of the two equilibrium structures appears in rapid equilibria [hydroxyphsophorane (XLVIII) ⇌ (LI)]. A decrease of temperature entails a successive upfield shift of the resonance peak until the attainment of a fixed position in the region characteristic of hydroxyphosphoranes[67] (Fig.1).

The opening of the five-membered ring and the formation of phosphtate isomers are catalysed by acids. On the other hand, the introduction of bases into the P(V) ⇌ P(IV) mixture favours the hydroxyphosphorane structure up to formation of stable hydrogen-bonded complexes or salts of hydroxyphosphoranes, which can be isolated.[65–68]

However, the structure of the cyclic skeleton of the molecules of hydroxyphosphoranes is of decisive importance for the increase of their stability. Hitherto stable hydroxyphosphoranes have been identified only for a series of spirocyclic phosphoranes made up of five-membered oxa- and dioxa-phospholan rings (the effect of the five-membered ring).[12,69] NMR evidence has been adduced for the formation of relatively unstable acyclic,[70] monocyclic,[71] and condensed bicyclic hydroxyphosphoranes[72] (Table 1).

The stability of hydroxyphosphoranes increases sharply up to the formation of the sole P(V) form in solutions after the introduction of electron-accepting oxo-groups [compounds (LII), (LIII), (LV), and (LVIII)] or trifluoromethyl groups [compounds (LVII) and (LIX)]. A significant stabilisation of hydroxyphosphoranes is ensured by the presence of geminal dimethyl, bis(trifluoromethyl), and diphenyl fragments in rings (the Ingold–Thorpe effect[2]).

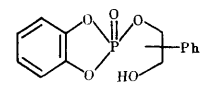
The estimation of the factors controlling the relative amounts of the forms involved in the hydroxyphosphorane ⇌ γ-hydroxyalkyl(aryl) phosphate equilibrium reduces, other conditions being equal, to the analysis of the sequence of equilibria (A) ⇌ (B) ⇌ (C) ⇌ (D) [Eqn.(3)]:[67]



(3)

The position of the hydroxyphosphorane–phosphate equilibrium is largely determined by two equilibrium constants—the dissociation constant K_1 and the cyclisation constant proper K_2, i.e. $K = K_1K_2$.[67] The determination of the thermodynamic parameters of the ring closure stage (B) ⇌ (C) (K_2) for compounds (XLVIII)–(L) with hydroxyacid ligands showed that the P(IV) form is slightly preferable for the cyclic oxo-compound (XLVIII) (ΔG^0 = +0.08, Table 2), whereas the spiran forms are more stable for the monosubstituted homologues (XLIX) and (L) under these conditions. The parameters obtained are close to those for other P(III) ⇌ P(V)[67] and P(V) ⇌ P(VI)[80] spirocyclisation processes.

The derivatives of the *gem*-disubstituted hydroxyacids (LII) and (LIII) and the phosphorane (LIV), synthesised with participation of benzohydroxamic acid, exist in the phosphorane forms over a wide temperature range (Fig.1). It is striking that the cyclic derivative of phenylethanediol (LX), whose structure is close to that of the spirophosphorane (LIV), does not pass to the spirophosphorane form under any of the conditions investigated. This has been attributed to the much lower dissociation constants K_1 of the phosphate (LX) compared with the phosphorylated derivative of benzohydroxamic acid (LIV):[67]



(LX)

The hydroxyphosphoranes (LVI)–(LVIII) containing endocyclic P–C bonds are exceptionally stable. These compounds have been isolated and exist as hydroxyphosphoranes in the crystalline state; the equilibrium with the phosphinate isomer is observed only in solutions of the tetrasubstituted hydroxyphosphorane (LVI).[69,76] The perfluoropinacone derivative (LIX) is so stable under the usual conditions that it can be easily recrystallised in the presence of moisture; the five-membered rings are not ruptured by sulphuric acid and potassium hydroxide.[79] In the latter case the poassium hydroxyphosphoranide is formed readily.

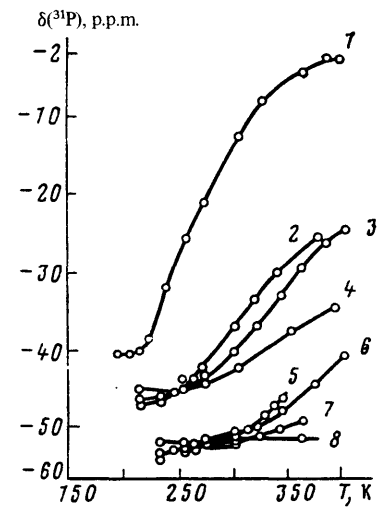


Figure 1. The influence of temperature on $\delta(^{31}P)$ for hydroxyphosphoranes:[67] 1) (XLVIII) (DMF); 2) (XLIX) (DMF); 3) (L) (DMF); 4) (LI) (DMF); 5) (LII) (CD_3CN); 6) (LII) (PhCN); 7) (LII) (DMF); 8) (LIII) (DMF); the numbering of the compounds is the same as in Table 1.

The XRD data for the triethylammonium salt of the hydroxyphosphorane (LIII)[74] and the salts of oligomeric hydroxyphosphoranes[75] confirmed that they have the TBP structure with five-membered rings in the *a* and *e* positions and the oxy-anion in the *e* position. The exocyclic P–O^- bond in these compounds is shortened, which reflects its double bond character.[73] This is caused in its turn by the influence of the oxo-group, as a result of which the phosphorus atom acquires a significant positive charge and the hydroxyphosphorane acquires fairly pronounced acid properties (Table 1).

Table 1. Stable hydroxyphosphoranes*.

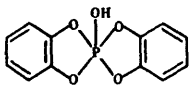
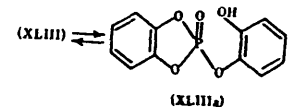
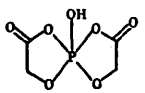
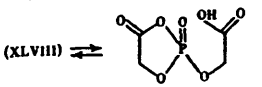
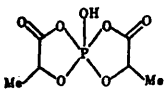
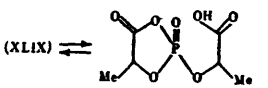
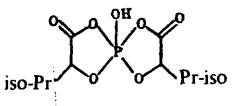
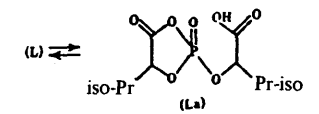
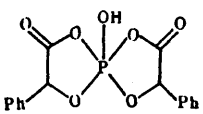
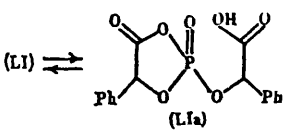
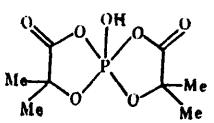
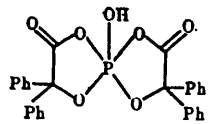
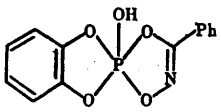
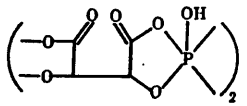
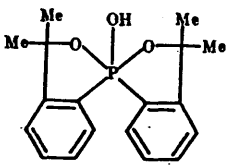
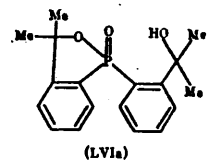
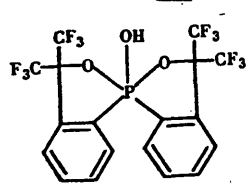
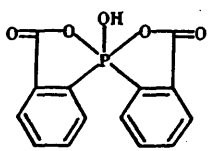
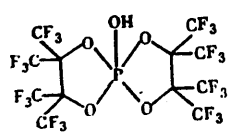
Hydroxyphosphorane	M.P. °C	pK_a(solvent)	$\delta(^{31}P)$, p.p.m. (solvent)	State in solution at room temperature	Refs.
 (XLIII)	—	9—10**	—27 (CD_3CN, —48° C)	 (XLIII) ⇌ (XLIIIa)	[64, 66]
 (XLVIII)	—	<3.5**	−13 (DMF)	 (XLVIII) ⇌ (XLVIIIa)	[67]
 (XLIX)	—	<3.5**	−37.4 (DMF)	 (XLIX) ⇌ (XLIXa)	[67]
 (L)	—	<3.5**	—43.5 (CD_3CN)	 (L) ⇌ (La)	[67]
 (LI)	—	3.5**	−42.8 (DMF)	 (LI) ⇌ (LIa)	[67]
 (LII)	—	2.5 (DMSO) 4.0 (DMF)	−52 (DMF)	[LII]	[67, 73, 74]

Table (cont'd).

Hydroxyphosphorane	M.P., °C	pK_a(solvent)	$\delta(^{31}P)$, p.p.m. (solvent	State in solution at room temperature	Refs.
 (LIII)	—	−0.6 (DMSO) 1.7 (DMF)	−52 (DMF)	(LIII)	[67, 73, 74]
 (LIV)	—	—	−23 (DMF)	(LIV)	[67]
 (LV)	—	−0.5 (DMSO)	−44 (DMF)***	(LV)	[73—75]
 (LVI)	181	10—11**	−26.3 (CH_3OD, −10° C)	(LVI) ⇌  (LVIa)	[69, 76]
 (LVII)	168	5.3	−17.8 (THF)	(LVII)	[76, 77]
 (LVIII)	266—269	5.3**	−38.5 ($CDCl_3$)	(LVIII)	[77, 78]
 (LIX)	72	2.0	−34.5	(LIX)	[79]

*The Table includes data up to 1984 for hydroxyphosphoranes isolated in a pure state or identified in solution by ^{31}P NMR.
**Approximate estimate.
***$\delta(^{31}P)$ for oligomers: −45 for the complex of the trimer with DMSO; −42.5 for the complex of the pentamer with trimethylamine.[75]

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

The fact that XRD data[63,66] for the hydroxyphosphinate (XXXVII) and the hydroxyphosphate (XLIV) confirm the favourable entropy of the hydroxyphosphorane ring closure is striking. The hydroxy-group in the 2-position in the alkylene (arylene) ether group is in direct proximity (~3 Å) to the P(IV) atom.

Table 2. Thermodynamic parameters of the equilibrium P(IV) ⇌ P(V)–O⁻.[67]

Compound	ΔH^0, kcal mol^{-1}	ΔS^0, e.u.	ΔG^{0*}, kcal mol^{-1}
(XLVIIIa)	−3.9	−13	+0.08
(XLIXa)	−5	−13	−1
(La)	−4.8	−11	−1.3

* 30° C.

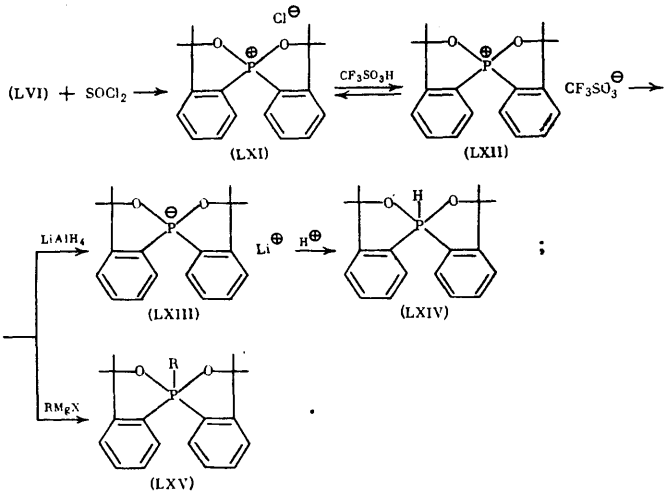
The isolation of stable hydroxyphosphoranes permitted well-founded inferences about their acid properties. This problem is of fundamental importance because hydroxyphosphoranes are partial esters of the hypothetical pentacoordinate phosphorus acid $P(OH)_5$.[81] At different stages of the investigation of hydroxyphosphoranes, their acid properties were estimated within wide limits—from pK_a = 10–11 [64,66] to claims that the strength of these acids is fairly high.[65] The latter were based on the ability of hydroxyphosphoranes to form stable hydrogen-bonded complexes with dimethylformamide (DMF) and dimethyl sulphoxide (DMSO) and ammonium salts with tertiary amines.[65,67,68]

Indeed direct determination of the pK_a (Table 1) demonstrated their fairly marked dependence on the character of the substituents. It was found that the dissociation constants of the oxo-substituted hydroxyphosphoranes (LIII) and (LV) are higher than those of the strong dichloroacetic and diphenylphosphoric acids.[73–75] As expected, in the general case the acid properties of the hydroxyphosphoranes increase sharply after the introduction of electron-accepting substituents into the five-membered rings (Table 1).

The study of the comparative reactivities of the hydroxyphosphoranes (LVI)–(LVIII) also demonstrated a significant role of the nature of the substituents in the ring. Whereas the methylated derivatives (LVI) is readily converted into the quasi-phosphonium compound (LXI) on treatment with thionyl chloride, the analogous salts are not formed from compounds (LVII) and (LVIII). In these cases the electron-accepting ring substituents apparently destabilise the positive charge on the phosphorus atom. On the other hand, the difference between the acid strengths is such that the sodium salt of the acid (LVII) can be formed on treatment with alkali, whereas compound (LVI) is deprotonated only with sodium hydride. The oxo-analogue (LVIII) is converted into a phosphorus(IV) derivative in aqueous alkaline solutions.[69]

The anion exchange between compound (LXI) and trifluoromethanesulphonic acid leads to the triflate (LXII); the latter is reduced to the phosphoranide anion (LXIII), which gives rise to the hydroxyspirophosphoranes (XLIV) on acidification. It is of interest that the first representatives of hydroxyphosphoranes have been obtained by oxidising hydrophosphoranes.[65,67] Alkylation (arylation) of the cations (LXII) with Grignard reagents affords the alkyl(aryl)spirophosphoranes (LXV).[69]

The description of the TBP structure of hydroxyphosphoranes is based on the concept of hypervalent bonds: the apical and central atoms of the TBP are linked by a three-centre four-electron delocalised bond, which consists of one unoccupied and two occupied MO made up of a single *p* orbital of each atom involved in the hypervalent bond.[69,82] Such a structure presupposes the presence of long bonds between the electronegative *a*-atoms and the central atom carrying a partial positive charge.



The stability of the TBP increases after the introduction of electron-accepting substituents at the *a*-atoms and is increased by the five-membered ring and Ingold–Thorpe effects. It is believed[69,82] that a significant difference between the electronegativities of the *a*- and *e*-atoms, which is achieved by introducing σ-donor carbon-centred or p_π-donor heteroatomic equatorial ligands, is an important factor stabilising hypervalent structures. It has also been suggested[79] that steric shielding by bulky substituents, for example trifluoromethyl substituents in the structure of compound (LVII), can also promote an increase of the stability of such systems. This is evidently likewise true of hypervalent compounds of other elements (S, Si, I).[82]

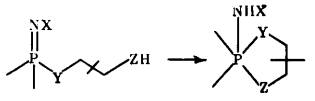
The importance of the synthesis and study of the structure and properties of hydroxyphosphoranes goes beyond the framework of the investigation of this new class of OPC alone. After the isolation and identification of hydroxyphosphoranes, the hydroxyphosphorane concept and the hypothesis of the role of phosphorus(V) intermediates in the nucleophilic substitution reactions at P(IV) received powerful experimental support. Data for the new type of phosphorus(V) acids combined with data for the strong acids of tetracoordinate phosphorus and weak acids of tricoordinate phosphorus constitute an integral picture of the complex problem of the relation between the structure and acidity of organophosphorus acids. It is extremely significant that the pathways leading to the approach to hydroxyphosphoranes presupposes the "opening" of the very strong (120–150 kcal mol^{-1} [83]) P=O bond (in essence addition to the P=O bond). Apparently energy is then gained as a result of the spirocyclisation of the reaction products.[2,69,76] This makes it necessary to look again at the character of the driving forces in many reactions of OPC: it may be that the formation of strong P=O bonds (or their analogues), as, for example, in the Arbuzov or Wittig reactions, is not the only factor which

determines the energy relations of chemical processes involving OPC and that account must be taken also of other factors, for example, the spirocyclisation and the effects accompanying it (see above).

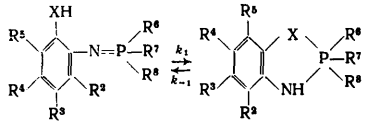
IV. AMINOPHOSPHORANES. THE PHOSPHIMIDE–PHOSPHORANE TAUTOMERISM

As stated above, the P=O double bond can participate in the addition reactions of H-containing nucleophiles with formation of hydroxyphosphoranes. In intermolecular addition reactions [Eqn.(1)] the latter are not detected—the interaction models the first stage of the nucleophilic substitution process at the tetrahedral phosphorus atom [$S_N2P(IV)$] which proceeds via an addition-elimination mechanism. Intramolecular addition to the P=O bond, particularly when it is accompanied by spirocyclisation, in some cases leads to stable hydroxyphosphoranes and this principle can evidently serve as the basis of the synthesis of stable cyclic phosphoranes.

Indeed the intramolecular addition of the γ-ZH functional group in alkoxy- or aryloxy-substituents to the P=N bond of phosphorus imides makes it possible to obtain stable aminophosphoranes (see Cherkasov et al.[2] and the literature quoted therein):



The intramolecular addition reactions involving the phosphimino-group and leading to spirocyclic aminophosphoranes are as a rule irreversible (see, however, Dahl et al.[84]), whereas in the series of monocyclic λ^5-diaza- and λ^5-oxazabenzophospholans it is possible to observe the ring–chain phosphimide–phosphorane tautomerism [Eqn.(4)] after the appropriate selection of substituents at the phosphorus and nitrogen atoms and in the benzene ring:



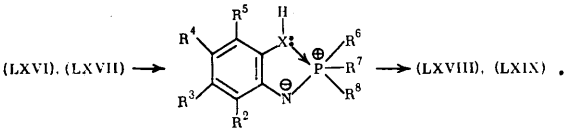
(4)

(LXVI): X = O; (LXVII): X = NR^1 (LXVIII): X = O; (LXIX); X = NR^1.

The study of the thermodynamics of equilibrium (4) in several reaction series[85–87] demonstrated the appreciable influence of temperature and of the nature of the solvent on the ratio of the tautomeric forms. Thus in nitrobenzene more than 90% of the acyclic phosphorus(IV) is present in the equilibrium mixture, whereas in tripropylamine the degree of cyclisation reaches 100%. With decrease of temperature, the equilibrium constant $K = k_1/k_{-1}$ increases [the content of the cyclanes (LXVIII) and (LXIX) increases].

The electronic influence of substituents is clearly shown when the groups in the phosphorus and imine components of the molecules are varied. Hydrogen atoms at the phosphorus atom fully displace the equilibrium towards aminophosphoranes. Electron-donating substituents in the imine fragment (R^3 = t-Bu) favour the phosphorus(V) form, while electron-accepting substituents ($R^3 = Ph_3C$) increase the content of the phosphimides (LXVI) in the tautomeric mixture.[85]

Thus the enhancement of the electron-donating properties of the atom X (O and N) to which a mobile hydrogen atom is attached and of the electron-accepting properties of the phosphorus atom promotes cyclisation. This is seen particularly clearly in the diazaphospholan series:[87] the NMR spectra of *N*-unsubstituted acyclic phosphimides (LXVII), R^1 = H, show only the phosphorus(IV) signal. These results are satisfactorily consistent with the mechanism involving the nucleophilic addition of the heteroatom X to the phosphorus atom in the cyclisation process.[85]



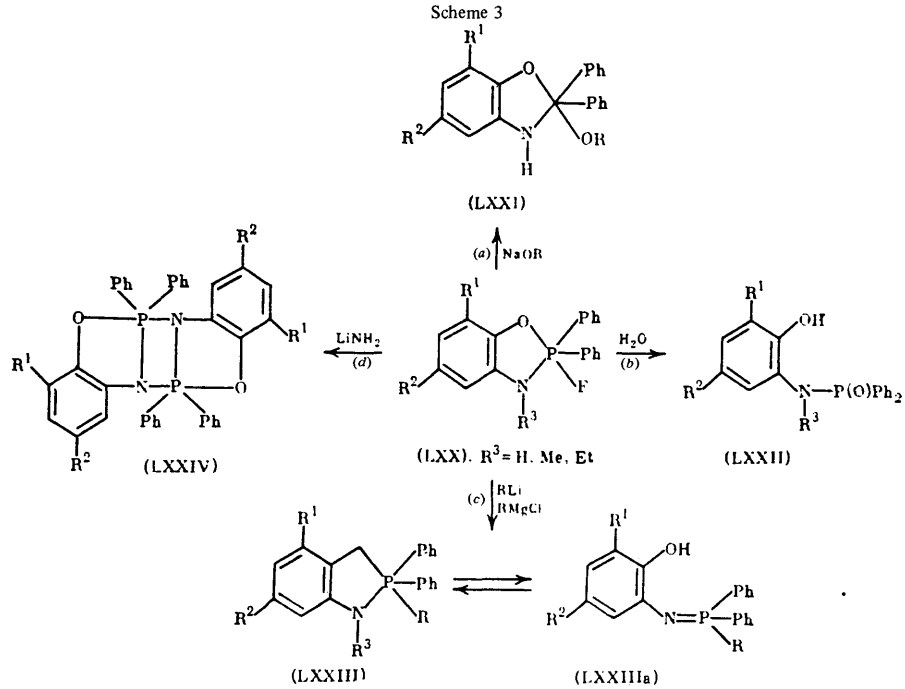
However, the steric characteristics of the substituents play a decisive role. In the series of oxaza-derivatives the equilibrium (LXVI) ⇌ (LXVIII) is displaced towards λ^5-oxazaphospholans only for R^4 = t-Bu.[85,86] Appreciable amounts of the phosphoranes (LXIX) appear in the mixture when the free rotation of the phosphimino-group in phosphimides is hindered (R^2 = t-Bu).[87]

This reaction series also illustrates the spirocyclisation effect which stabilises the phosphorus(V) form. The inclusion of phosphorus atoms in the five-membered ring, as in compound (LXVII, $R^7 = R^8$ = 2,2′-biphenylene), makes it possible to detect appreciable amounts of λ^5-diazaphospholans in the mixture even in those cases where the nitrogen atom is unsubstituted (R^1 = H).[87]

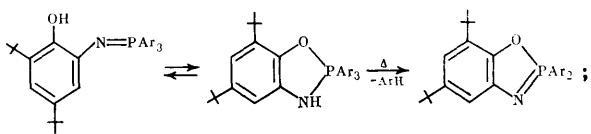
The observed features of the interconversions of phosphimides and aminophosphoranes are also manifested in the synthetic results of certain reactions of λ^5-oxazaphospholans.[88] Thus the ligand exchange of fluorine in the aminofluorophosphorane (LXX) for an alkoxy-group (Scheme 3, reaction *a*) does not alter the coordination of the phosphorus—the phosphorane (LXXI) is obtained, while hydrolysis (reaction *b*) leads to the phosphinamidate (LXXII) and not to an aminohydroxyphosphorane. The substitution of the fluorine atom by carbon-centred nucleophiles (reaction *c*) for R^3 = H induces the appearance of a mixture of products [(LXXIII, R^3 = H) ⇌ (LXXIIIa)]; when R^3 = alkyl, such tautomerism is naturally impossible and the only reaction product is the λ^5-oxazaphospholan (LXXIII, R^3 = Me or Et). The interaction of compound (LXX) with lithium amides (reaction *d*) leads to diazadiphosphetidines (LXXIV), evidently via the stage involving the formation of the phosphimine (LXXVI) with an endocyclic P=N bond:[88]†

† For information about the ease of dimerisation of cyclic phosphimides, see Dahl et al.[84] and Sheldrick et al.[89] and the literature quoted therein.

Scheme 3



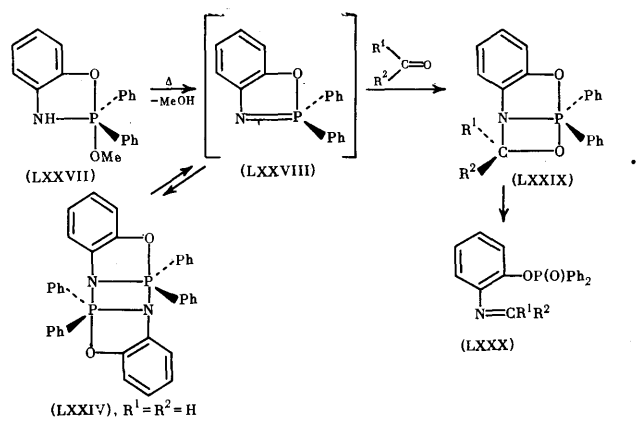
The phosphimides (LXXVI, a and b) are also formed when the phosphimides (LXXV, a and b) are heated above the melting point, which is accompanied by the evolution of the corresponding hydrocarbons:[90]



(LXXV, a and b) (LXXVI, a and b)

Ar = Ph (a), *n*-MeC_6H_4 (b)

The ability of cyclic aminophosphoranes to be converted into phosphimides has found a synthetic application in the reactions with carbonyl compounds.[91] The interaction of phosphorane (LXXVII) with aldehydes, ketones, and formamides proceeds via a stage involving the formation of the phosphimide (LXXVIII), which is converted into the phosphinates (LXXX) via a mechanism analogous to that of the Wittig reaction:

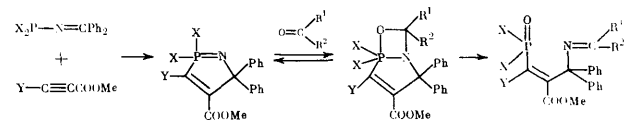


(LXXVII) (LXXVIII) (LXXIX) (LXXX)

(LXXIV), $R^1 = R^2 = H$

The formation of the phosphimide (LXXVIII) has been confirmed by the isolation of its dimer (LXXIV, R^1, R^2 = H) on thermolysis of compound (LXXVII) in solution or in the liquid state. The formation of the same final products (LXXX) as a result of the reaction of diazaodiphosphetidine (LXXIV) with carbonyl compounds indicates the reversibility of the dimerisation reaction (LXXVIII) ⇌ (LXXIV).

The transition state (LXXIX) (or the intermediate) in these reactions is modelled by the stable adducts (LXXXII, R^1 = Me or CF_3; R^2 = Me, CF_3 or Ph), obtained and isolated as a result of the consecutive [2 + 2]-cycloaddition reactions,[89,92] accompanied by a change in the coordination number of the phosphorus atom [P(III) → P(IV) in compound (LXXXI) and P(III) → P(V) in compound (LXXXII)]:



(LXXXI) (LXXXII) (LXXXIII)

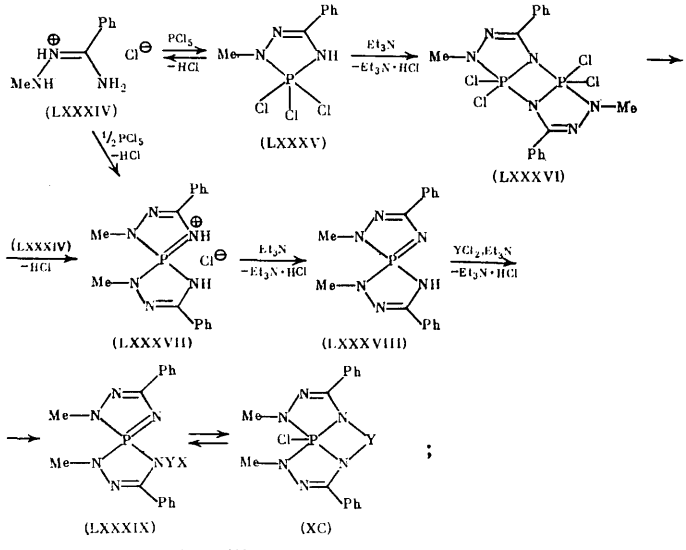
The stability of the cyclic adducts (LXXXII) with an aminophosphorane structure increases with decrease of temperature and with increase of solvent polarity. Acyclic phosphimides do not give rise to stable aminophosphoranes in their reactions with carbonyl compounds.[89]# The influence of the electron-accepting properties of the substituents in the carbonyl partner must also be optimal: the equilibrium in the reaction with acetone is wholly displaced towards the initial compounds. The adducts (LXXXII, $R^1 = CCl_3$, R^2 = H) with chloral and (LXXXII, $R^1 = C_6H_4NO_2$-*p*, R^2 = H) with *p*-nitrobenzaldehyde are converted into the aldiminophosphine oxides (LXXXIII, R = CCl_3 or $C_6H_4NO_2$-*p*, R^2 = H) with rupture of the phosphimide bond even at room temperature.

A version of the [2 + 2]-cycloaddition of hexafluoroacetone to an unstable phosphimide with an exocyclic P=N bond has been discussed by Storzer et al.[93]

The driving force of the cycloaddition reaction is the reduction of the angular strain in the TBP of the phosphorane (LXXXII) compared with the phosphimide (LXXXI). According to XRD data,[89] the structure of the phosphorane (LXXXII) deviates only slightly from the ideal TBP, whereas the initial compound (LXXXI), in which the endocyclic CPN angle differs greatly from the tetrahedral value, is destabilised by an appreciable steric strain.[92]

Interesting P(IV) ⇌ P(V) interconversions have been observed in the series of spirocyclic tetraaminophosphoranes.[94] The thermal condensation of equimolecular amounts of *N*-methylbenzamidrazone hydrochloride (LXXXIV) with phosphorus pentachloride leads to diaminotrichlorophosphorane (LXXXV), which is converted into the diazadiphosphetidine (LXXXVI) on treatment with bases. The same reaction with a twofold excess of compound (LXXXIV) is completed by the formation of the immonium chloride (LXXXVII); the latter is dehydrochlorinated by a tertiary amine to the spirocyclic phosphazene (LXXXVIII). The same compound can be arrived at by treating the dimer (LXXXVI) with the initial compound (LXXXIV) (Scheme 4):[94,95]

Scheme 4



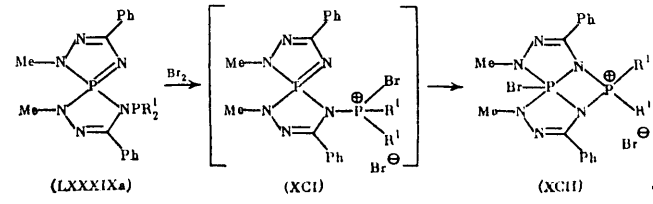
On passing from compounds (LXXXV) and (LXXXVI) to the spirocyclanes (LXXXVII) and (LXXXVIII), the phosphorus atom becomes a weaker electron acceptor (replacement of two chlorine atoms by amino-groups), so that the triaminophosphazene (LXXXVII) has an ionic structure, in contrast to the diamine analogue (LXXXV), and its dehydrochlorination product is monomeric [cf. the transition (LXXXV) → (LXXXVI)].

Phosphorylation of the phosphazene (LXXXVIII) by dichlorophosphines and dichlorophosphine oxides enabled Schmidpeter et al.[94] to observe a new type of reversible P(VI) ⇌ P(V) transitions—the phosphazene–diazadiphosphetidine rearrangement, involving the migration of chlorine (and not of a proton as in the previous examples) between the P(III) and P(IV) atoms in compound (LXXXIX) and an increase of the coordination number of one of the phosphorus atoms in compound (XC). This is accompanied by a pronounced shift of the $\delta(^{31}P)$ signal from ~50 p.p.m. for the P(IV) atoms in compound (LXXXIX) to −10 to −40 p.p.m. for the phosphorane phosphorus in compound (XC), the P(V) chemical shift depending significantly on the structure of the fragment Y.

The position of the tautomeric equilibrium is also determined by the nature of the P substituent in the fragment Y: the stronger the electron-accepting properties of the P(III) in the tricyclic tautomer (XC), the greater the shift of the equilibrium towards this tautomer. For the group Y = PPh, the tautomer (XC) is not detected and the introduction of the dimethylamino-group at P(III) lowers appreciably the content of the phosphorane: at room temperature in chloroform the ratio (LXXXIX) : (XC) is 73 : 27 for Y = $PNMe_2$.

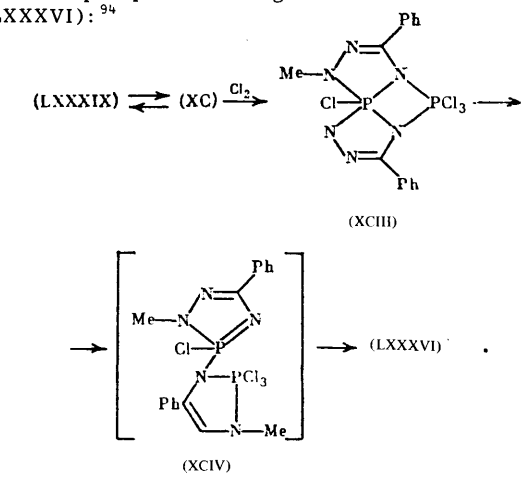
Each of the tautomeric forms (LXXXIX) and (XC) is chiral and can exist as two diastereoisomers and therefore in the general case four isomers may be present in the equilibrium mixture.[94] Thus, when crystalline compound (XC, Y = PCl) (one stereoisomer) is dissolved in chloroform, only a mixture of the diastereoisomers of compound (XC) in proportions of 92 : 8 is initially observed but after a week a mixture of three isomers is detected in the solution—one isomer of compound (LXXXIX) and two isomers of compound (XC) (32 : 63 : 5). The equilibrium mixture of the four isomers of compounds (LXXXIX) and (XC) with Y = POPh in benzene (17 : 30 : 27 : 26) is converted into a single crystalline isomer (XC, Y = POPh) after the removal of the solvent.[94]

It is of interest that the isomerisation described above takes place not only as a rsult of the transfer of a halogen between the P(III) and P(IV) atoms but also in the phosphazene–phosphonium system:[94]

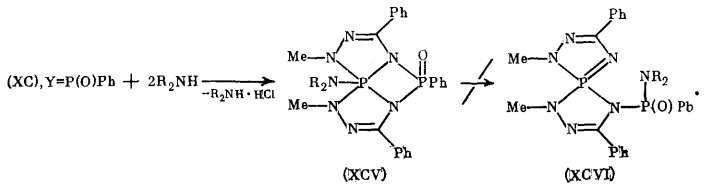


Bromination of the phosphazenes (LXXXIXa, R^1 = Ph or NMe_2) leads to tricyclic phosphorane–phosphonium isomers (XCII) and not to the expected spirophosphorane phosphazene–phosphonium isomers (XCI).

An even more complex reorganisation of the molecules takes place as a result of the bromination of the mixture of compounds (LXXXIX) and (XC, Y = PCl). The diphosphorane (XCIII), which exists only for a short time in solutions, undergoes in succession two types of isomerisation—the skeletal rearrangement to the hypothetical phosphazene (XCIV) as a result of the opening of the four-membered ring with transfer of the hydrazone group and subsequent closure of a new diazadiphosphetidine ring with formation of the dimer (LXXXVI):[94]



The amination of the halogenophosphoranes (XC) with ammonia, primary or secondary amines, and hydrazine leads to stable pentaaminophosphoranes (XCV) which are incapable of the P(V), P(IV)⇌P(IV), P(IV) tautomerism:



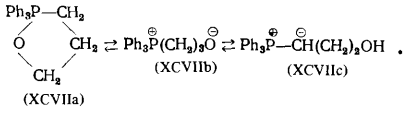
(XCV) (XCVI)

On reaction with aldehydes and ketones, the hydrazide [XCV, R_2N = N(He)NH_2] is converted into the corresponding hydrazones. It has been noted[94] that compounds of pentacoordinate phosphorus linked to five N-ligands as a rule tend to be converted into phosphorus(IV) derivatives. For example, the substitution of the halogen atoms in the dimer (LXXXVI) by amino-groups induces its conversion into the monomeric form.[95] In this sens compounds (XCV), which are not converted into the isomeric phosphonatophosphimides (XCVI), constitute a fairly rare example of stable pentaaminophosphoranes. §

V. OTHER TAUTOMERIC TRANSFORMATIONS OF PHOSPHORANES. PHOSPHOROTROPIC PROCESSES

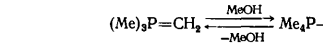
Various types of tautomeric transformations into compounds of tricoordinate, tetracoordinate, pentacoordinate, and hexacoordinate phosphorus have been observed for compounds of pentacoordinate phosphorus. Equilibrium transitions between compounds of pentacoordinate and dicoordinate phosphorus are so far unknown. The discovery and investigation of the phosphite–phosphorane and phosphimide–phosphorane tautomerism indicates the relative ease of the dissociation of the P=O and P=N bonds and the stability of the phosphoranes arising in such a process. All these equilibrium processes are characteristic only of cyclic, mainly λ^5-1,3,2-diheterophospholan, systems; in this case there is no analogy with acyclic compounds.

The dissociation of the P=C bond with formation of a phosphonium centre also proceeds fairly readily but the phosphorane–ylide equilibrium could not be observed for a long time, although some examples of the dual (both as a phosphorane and as an ylide) behaviour of phosphorane systems have been noted. Thus the λ^5-1,2-oxaphospholan (XCVII) has the structure of a compound with a pentacoordinate phosphorus atom (XCVIIa), but in some reactions it behaves as the betaine (XCVIIb), while in reactions with aldehydes and ketones it also reacts as a phosphonium ylide (XCVIIc):[97,98]

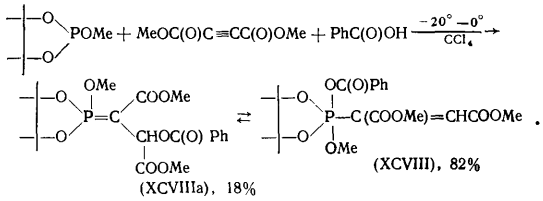


(XCVIIa) (XCVIIb) (XCVIIc)

The equilibrium between an ylide and a phosphorane has been reported but it is associated with the addition-elimination of the methanol molecule:[99]



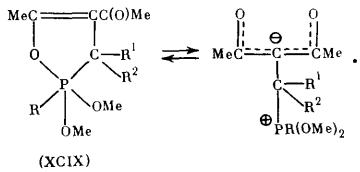
The first piece of evidence for the existence of the ylide–phosphorane equilibrium has been obtained[100] in a study of the interaction of cyclic phosphites with acetylenedicarboxylate ester in the presence of benzoic acid:



(XCVIIIa), 18% (XCVIII), 82%

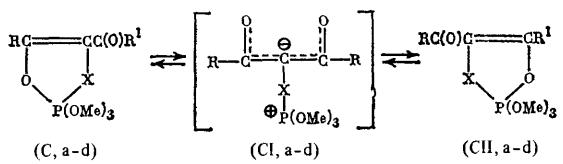
In methylene chloride the fraction of compound (XCVIIIa) increases to 37%, but, after the removal of this solvent and dissolution in CCl_4, the previous ratio is restored.

The phosphorane–phosphonium betaine tautomerism has been postulated for the monocyclic λ^5-1,2-oxaphospholens (XCIX) on the basis of the exchange of the methyl groups of the acetylacetonate system observed from ^{1}H NMR spectra.[3,4,10,101] An analogous phenomenon was believed[102,103] to be characteristic also of spirophosphorane systems:



(XCIX) (5)

The existence of the two tautomeric forms (Ca) and (CIIa), observed in solutions at room temperature [the ratio (Ca) : (CIIa) = 1 : 2 and is independent of the nature of the solvent], is apparently associated with the appearance of an intermediate dipolar ion (CI), which, however, is not detected in the spectra owing to its short life span:[104–106]



(C, a-d) (CI, a-d) (CII, a-d) (6)

(a) R=Ph; R^1 = Me; X = CHPh, $CHC_6H_4NMe_2$-*p*, $CHC_6H_4NO_2$-*p*;
(b) R = Me; R^1 = Me; X = CHMe, CHPh, $CHC_6H_4NMe_2$-*p*, $CHC_6H_4NO_2$-*p*;
(c) R = R^1 = Ph; X = O; (d) R = R^1 = Ph; X = NPh

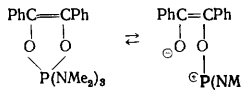
Detailed studies of the ^{1}H, ^{13}C, and ^{31}P NMR spectra of the (C, a–d)–(CII, a–d) systems as a function of temperature showed than an intramolecular transfer of the phosphorus-containing group takes place in such systems between two oxygen atoms;[107,108] the tautomeric process is degenerate for the phosphoranes (C, b–d)–(CII, b–d).

The chemical shifts of the phosphorus nuclei in all the solvents[107,108] remain unchanged over a wide temperature range (from −35° to +125 °C) and are observed in the regions characteristic of the resonance of the nuclei of pentacoordinate phosphorus(−27 to −51 p.p.m.). Thus the phosphonium structure is not an equilibrium component of these systems—the equilibrium is between two phosphorane forms

§ The synthesis of other aminophosphoranes containing two phosphorus atoms with different types of coordination has been described.[96]

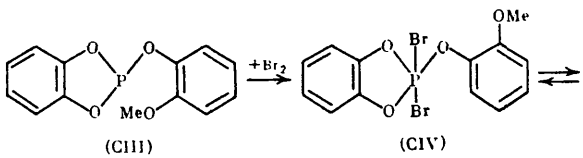
Eqn.(6) and the phosphorane–phosphonium tautomerism [Eqn.(5)] is not observed for compounds of this kind. The temperature-induced changes in the NMR spectra of phosphoranes described in other investigations[3,4,101–103] should apparently be interpreted analogously.

For exactly the same region, it is impossible to give an unambiguous answer concerning the possibility of the phosphorane–phosphonium equilibrium in aminophosphoranes:[101,109,110]

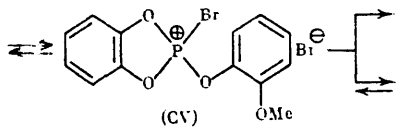


Detailed study of these systems by ^{1}H, ^{13}C, and ^{31}P NMR over a wide temperature range in solvents of different polarity led the authors[111,112] to the conclusion that the observed spectral changes are associated with the different polarities of the P–O bond, which depend on the dielectric constant of the medium.

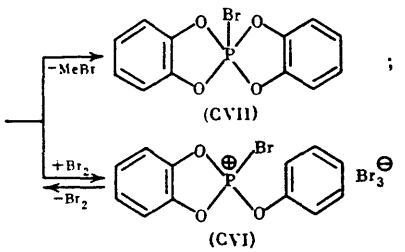
The existence of the equilibrium between the phosphorane and phosphonium structures has been demonstrated by low-temperature ^{13}C NMR in a study of the halogenation of the cyclic phosphite (CIII):[113]



(CIII) (CIV)



(CV)

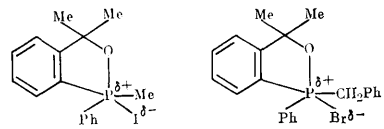


(CVII) (CVI)

At low temperatures (−100 °C) the dibromophosphorane (CIV) [$\delta(^{31}P)$ = 110 p.p.m.] and the phosphonium tribromide (CVI) (35 p.p.m.) were detected. The intermediate bromide (CV) ultimately symmetrises to form bromospirodiphenylenetetroxyphosphorane (CVII) (−28 p.p.m.); in essence this is an unusual version of the Arbuzov reaction, the second stage involving the dealkylation of the alkoxy-group separated from the phosphorus atom by the phenoxy-bridge. The driving force of this version of the Arbuzov reaction is spirocyclisation to compound (CVII) (see Section III) and not the formation of the thermodynamically favourable P=O bond as in the classical Arbuzov reaction.

The phosphorane–phosphonium equilibrium is characteristic also of acyclic phosphoranes. In acyclic systems this equilibrium is as a rule displaced towards the phosphonium form, while in cyclic systems it is displaced towards the phosphorane form, owing to the pronounced ring strain arising in cyclic, specially spirocyclic, phosphonium cations. Thus only the product with pentacoordinate phosphorus has been detected on chlorination of ethylene phosphorochloridite.[114]

The structure of the monocyclic phosphoranes (CVIII) and (CIX) is intermediate between the halogenophosphorane and phosphonium halide structures:[115,116]

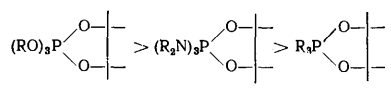


(CVIII) (CIX)

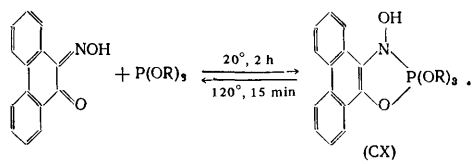
The appreciably ionic character of the phosphorus–halogen bond shifts the $\delta(^{31}P)$ signals of these compounds to the region characteristic of phosphonium structures, while the *ortho*-protons of the aromatic ring and the diastereotopic benzyl protons in compound (CIX) are manifested in the "phosphorane" region. By varying the substituents at the phosphorus atom, it is possible to alter the polarity of the phosphorus–halogen bond, whereupon the ^{1}H NMR spectra of such structures become characteristic in many cases of ionic compounds. This behaviour is very close to that observed for the NMR spectra of the adducts of α-dicarbonyl compounds with tris(amino)phosphines.[111,112]

VI. THERMOLYSIS OF PHOSPHORANES

It has already been stated that the stability of λ^5-1,3,2-diheterophosphacyclanes increases in the sequence acyclic < monocyclic < spirocyclic. This is valid also for their thermal stabilities. The series based on the influence of exocyclic groups at the phosphorus(V) atom on the thermal stabilities of monocyclic phosphoranes has been established:[117]



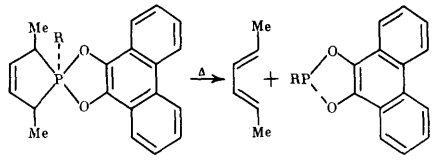
Many cyclic phosphoranes have such high thermal stabilities that they can be vacuum distilled, but some phosphoranes, obtained from phosphites or their analogues and α-dicarbonyl or αβ-unsaturated carbonyl compounds, decompose on heating intot the initial reactants, which indicates the reversibility of their formation reactions.[118–121] The phosphoranes formed after prolonged heating (50–60 °C) of trimethyl phosphite with dibenzylideneacetone, benzylideneacetophenone, and benzylidene-α-tetralone dissociate into the starting materials at a higher temperature (>90 °C).[122,123] The thermolysis of λ^5-1,3,2-oxaphospholans (CX) also leads to the ready elimination of trialkyl phosphites and the regeneration of the initial *o*-quinone monoxime:[124]



(CX)

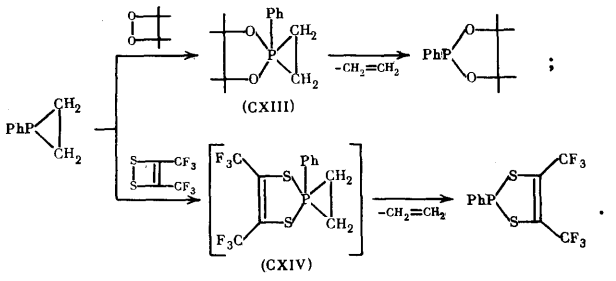
The rate of decomposition of λ^5-1,3,2-diheterophospholans is determined to some extent by the stereochemistry of the cyclic molecular skeleton.[125–128] Thus the study of the thermal decomposition of the stereoisomeric spirophosphoranes (CXI) established that steric factors exert a decisive influence on the rate of stereospecific fragmentation with formation of a diene and phosphonite (CXII): for the *cis*-disposition of the substituents R and Me in the phospholen ring, the decomposition proceeds much more readily; the bulky phenyl group at the phosphorus atom also accelerates the

fragmentation. The influence of electronic factors on this process is insignificant:[128]



(CXI) (CXII)

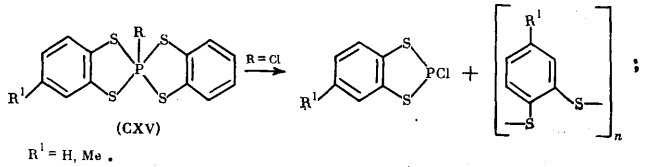
The thermal stability of λ^5-1,3,2-diheterophosphacyclanes varies within very wide limits depending on the structure of the rings and the nature of the substituents at the phosphorus atom (see Arbuzov and Polezhaeva[10] and the references quoted therein). As an example of extremely low stability, one may quote the spirophosphorane formed on interaction of phenylphosphiran with dioxetan.[129] The λ^5-dioxaphospholan (CXIII), containing a three-membered ring, is stable only at −80 °C; at room temperature it decomposes with elimination of ethylene. An analogous behaviour evidently obtains also in the case of the dithiaphospholen (CXIV):[130]



(CXIII) (CXIV)

These reactions involve a kind of "transcyclisation" of the phosphorus(III) derivatives.

Phosphoranes containing sulphur atoms linked directly to the phosphorus atom have been investigated much less than their oxygen analogues. The stability of the spiro-phosphoranes with four sulphur atoms (CXV) depends greatly on the exocyclic substituent R and decreases in the sequence Me > Ph ≫ Cl:

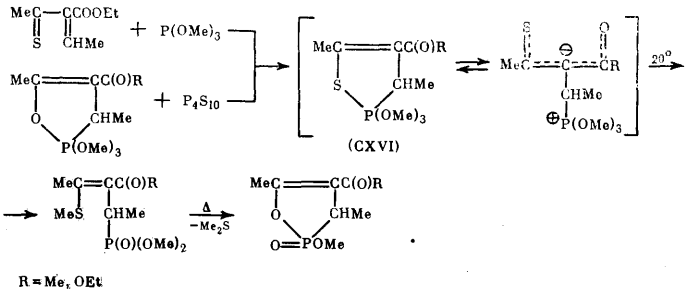


(CXV)

R^1 = H, Me.

Although in the latter case (R = Cl) the compound does form, it decomposes immediately with formation of oligomeric sulphides. The authors explain this instability by the unfavourable position of the chlorine atom in the e-position in the TBP or in the apical position of a square pyramid.[131]

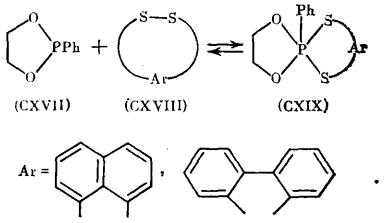
The monocyclic phosphoranes (CXVI) containing the 1,2-thiaphospholen ring cannot be isolated. They readily isomerise already in the course of their synthesis with migration of the methyl group to the nucleophilic sulphur atom:[132,133]



(CXVI)

R = Me, OEt

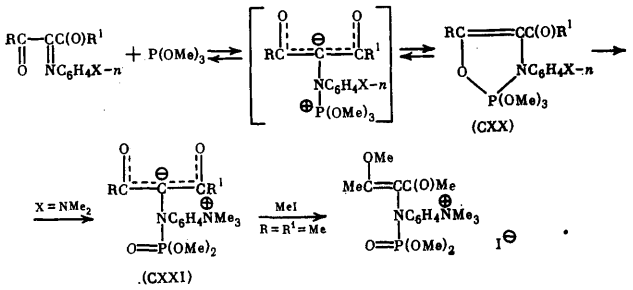
The first instance of reversible insertion in the disulphide linkage has been described.[134] The mode of the reaction of the cyclic phosphonite (CXVII) with the cyclic aromatic disulphides (CXVIII) depends on the nature of the solvent employed:



(CXVII) (CXVIII) (CXIX)

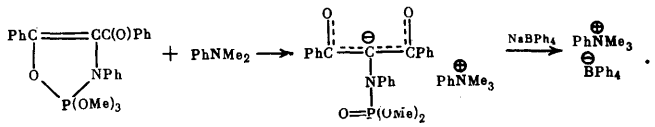
In acetonitrile the spirophosphoranes (CXIX) are formed readily and can be obtained in a crystalline state. In other media (CH_2Cl_2, $CHCl_3$) the reverse reaction predominates. Both processes proceed quantitatively without the formation of side products and are specific to the (CXVII) + (CXVIII) pair only.

The influence of the nature of the solvent on the stability of phosphoranes has been noted fairly frequently. The reversible formation reaction of the phosphoranes (CXX) has been observed for the interaction of 2-monoanils of 1,2,3-tricarbonyl compounds with trialkyl phosphites.[135–137] For X = H, the phosphorane (CXX) was isolated in a crystalline form. For X = NMe_2, the formation of phosphoranes in solution has been detected by ^{31}P NMR at room temperature. The attempts to isolate them in a crystalline state were unsuccessful: either the initial compounds are recovered (in ether) or the betaines (CXXI) are formed (in methylene chloride or in an excess of the phosphite). The betaines (CXXI), which are ammonium inner salts, are formed as a result of the O → N migration of the methyl group. The rearrangement of the phosphoranes into the stable betaine system, observed for the first time in Refs.135–137, shows that phosphoranes have the capacity to alkylate tertiary amines.

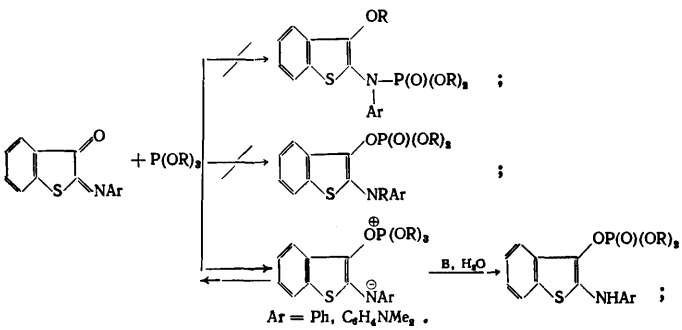


(CXXI)

This was also confirmed by the model reaction[138]

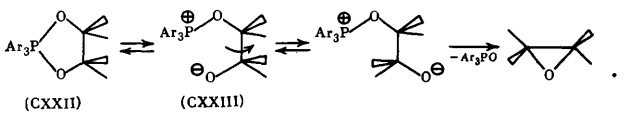


The monoanil of benzothiophen-2,3-dione does not react with trialkyl phosphites in a dry solvent; in the presence of moisture, the reaction proceeds via a protonation, but not alkylation, mechanism:[139]



Ar = Ph, $C_6H_4NMe_2$.

The thermolysis of λ^5-1,3,2-dioxaphospholans (CXXII) leads to the formation of epoxides with inversion of the configuration at the carbon atom[140-143] (see Arbuzov and Polezhaeva[10] and the references quoted therein). The mechanism of this reaction involves the heterolytic dissociation of the P–O bond, rotation about the C–C bond, and irreversible intramolecular substitution of the sp^3-carbon atom with formation of an epoxide:

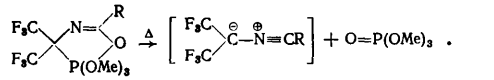


(CXXII) (CXXIII)

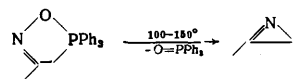
The study of the kinetics of these reactions by NMR [145] showed that they are of first order with respect to the phosphorane and that the thermolysis rate constants vary linearly with the σ constants of the substituents in the exocyclic aromatic groups (ρ = −3.5). The negative sign of ρ indicates the acceleration of the decomposition process with enhancement of the electron-donating properties of the varied groups, which facilitate the dissociation of the P–O bond and evidently stabilise the phosphonium centre in the intermediate (CXXIII).

At the same time the introduction of electron-donating groups should hinder the nucleophilic substitution reaction at the irreversible epoxide elimination stage, so that, when account is taken of effects which compensate one another, a fairly large absolute value of ρ is somehwat unexpected. The activation energy for the decomposition process (~20 kcal mol^{-1}) is close to that for the reactions of phosphoranes involving the rupture of the endocyclic P–O bond,[144] and the heterolytic dissociation reaction (CXXII) → (CXXIII) is therefore most important.[145]

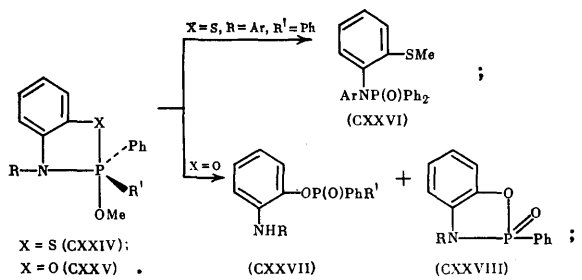
The thermal and photolytic decomposition of λ^5-1,4,2-oxazaphospholens leads to the formation of nitrile ylides[146] (see Arbuzov and Polezhaeva[10] and the literature quoted therein). Their formation was detected with the aid of dipolarophiles. The reaction with these substances leads to products of [3 + 2]- and [3 + 1]-cycloaddition:[147,148]



The pyrolysis of λ^5-1,5,2-oxazaphospholens is accompanied by the formation of azirines in high yields.[149] Bearing in mind the ready availability of such initial phosphoranes, which are obtained from α-bromoketones or ketoylides and triphenylphosphine, and also the possibility of carrying out all the stages without isolating the intermediates, the above method of synthesis of azirines can be regarded as fairly general and suitable for preparative purposes:



The formation of phosphoryl compounds on thermal decomposition of cyclic oxaphosphoranes has been frequently observed. The formation of compounds of tetracoordinate phosphorus as a result of thermal rearrangements of phosphoranes is rarer. Thus, on heating, the 1,3,2-thiazaphospholane (CXXIV) is converted into the phosphinamidate (CXXVI). On the other hand, the corresponding λ^5,1,3,2-oxazaphospholans (CXXV) are thermally very stable.[152] Their thermolysis in the gas phase[153] leads to the formation of products with retention [compound CXXVII)] or cleavage [compound (CXXVII)] of the oxazaphospholan ring depending on the character of the exocyclic substituents at the phosphorus atom: for R^1 = OMe, the main product is compound (CXXVIII), which has a cyclic structure:



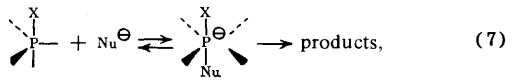
X = S (CXXIV); X = O (CXXV).

VII. NUCLEOPHILIC SUBSTITUTION AT A PENTACOORDINATE PHOSPHORUS ATOM

The mechanism of nucleophilic substitution reactions at a pentacoordinate phosphorus atom [S_N2P(V)] has not been studied in quite such detail as the mechanism of substitution reactions at a phosphorus(IV) atom. To some extent this is associated with the fact that the chemistry of phosphoranes has developed mainly during the last two decades. However, the main difficulty consists in the exceptionally high rates of hydrolysis (solvolysis) of phosphorus(V) compounds.

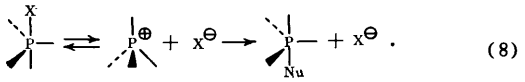
The kinetic study of these processes is complicated by the presence of a large number of stages—the reaction rarely stops after the rupture of one of the two bonds between phosphorus(V) and the heteroatom and usually develops further.

Two probable mechanisms of the $S_N2P(V)$ reactions have been discussed:[154–156] an associative mechanism involving hexacoordinate transition states and (or) intermediates:



(7)

and a dissociative mechanism with intermediate formation of phosphonium ions:



(8)

The study of the kinetics of the hydrolysis of pentaaryloxyphosphoranes demonstrated the exceptional sensitivity of the rate of reaction to the electronic and especially steric effects of the substituents at the benzene ring in neutral and alkaline media (Table 3).[154] The rate of reaction increases with enhancement of the electron-accepting properties of the substituent and is sharply retarded after the introduction of *ortho*-groups. This influence of the substituent X, the magnitude of the kinetic isotope effects (KIE) ($k_{H_2O}/k_{D_2O} = 3$ in hydrolysis by water and approximately unity in acid hydrolysis), and the absence of a salt effect are not characteristic of a dissociative process [Eqn.(8)] but agree well with the rate-determining attack by the water molecule or the hydroxide anion on the pentacoordinate phosphorus atom in pentaaryloxyphosphoranes:[154]

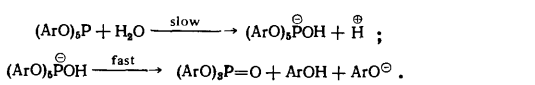


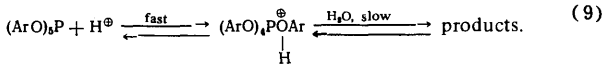
Table 3. Kinetics of the hydrolysis of pentaaryloxyphosphoranes $(XC_6H_4O)_5P$ at 25 °C in 25% dimethoxyethane.[154]

Reaction rate constant	X				
	H	*o*-Me	*p*-Me	*o*-Cl	*p*-Cl
k_{H_2O}, s^{-1}	0.202	$1.1\cdot10^{-5}$	0.0197	0.106	390
k_{H^+}, mol litre^{-1}s^{-1}	16.4	1.3	79	—	—
k_{OH^-}, mol litre^{-1}s^{-1}	11.4	$7.5\cdot10^{-4}$	3.4	—	—

Notation: k_{H_2O} is the rate constant for neutral hydrolysis ("plateau" on curve *2* in Fig.2), k_{H^+} the rate constant for acid hydrolysis (left-hand branch of curve *2*), and k_{OH^-} the rate constant for base hydrolysis (the right-hand branch of curve *2*).

An increase of the steric hindrance by the ligands destabilises the octahedral intermediate (or the transition state). By imparting a positive charge to the phosphorus atom, electron-accepting substituents accelerate the slow stage of the reaction, namely the attack by the nucleophile on the phosphorus(V) atom.

The acid-catalysed reaction proceeds with protonation of the phosphoranes and the subsequent rate-determining substitution of the phenol by water:



(9)

The acid hydrolysis reaction is less sensitive to the influence of substituents but in this case too the steric effect of the group X is manifested distinctly by a decrease of k_{H^+} (Table 3). The rate of reaction varies linearly with the concentrations of H^+ and OH^- in the strongly acid and strongly alkaline media respectively (Fig.2).

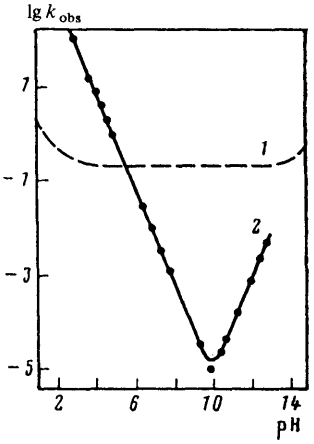
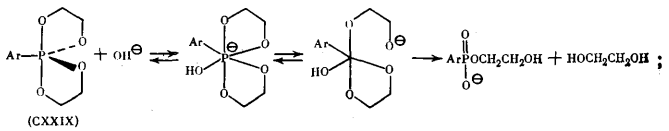


Figure 2. Dependence of the rate of hydrolysis of phosphorane (k_{obs}) on the pH of the medium: 1) penta-aryloxyphosphoranes; 2) spirophosphoranes (CXXIX).[154,155]

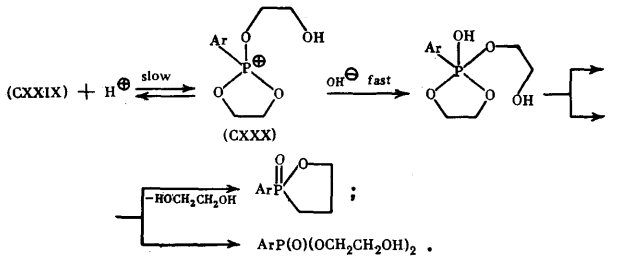
Another type of influence of the pH on the rate was established in a study of the kinetics of the hydrolysis of spirocyclic phosphoranes.[155] The alkaline reaction (in the pH range pH > 10, Fig.2) of the phosphoranes (CXXIX) is also described satisfactorily within the framework of the associative mechanism. In these reactions, involving the opening of the rings in λ^5-1,3,2-dioxaphospholans, and also in exocyclic substitution reactions involving alkoxy(aryloxy)-spiro-phosphoranes,[156] an increase of the reactivity of the organophosphorus substrates is observed after the introduction of electron-accepting substituents into the ligands.

However, in the range pH < 9 the hydrolysis of compound (CXXIX) resembles very closely the analogous reactions of dioxolan orthoesters, for which a dissociative carbonium mechanism has been established. It has been suggested[155] that the experimental results agree best with the acid-catalysed rate-determining dissociation reaction (CXXIX) ⇌ (CXXX) and the rapid cleavage of one or both rings:



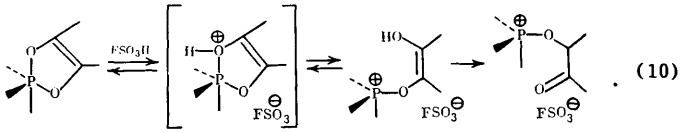
(CXXIX)

Ar = C_6H_4Me-*p*, Ph, C_6H_4Cl-*p*.



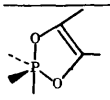
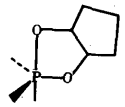
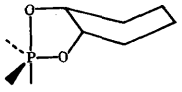
The pre-equilibrium protonation of the neutral oxaphosphorane (CXXIX) takes place with the simultaneous rupture of the P–O bond, so that the existence of the protonated phosphorane [Eqn.(9)] as an intermediate in cyclic systems is not obligatory.[155] This may be associated with the considerable ring strain in the protonated cyclic phosphorane. In this sense the acid hydrolysis of the phosphoranes (CXXIX) resembles the nucleophilic substitution reactions of five-membered cyclic phosphates.[2,157] It is believed[156] that in the general case the contribution of the dissociative mechanism should increase with enhancement of the electron-accepting properties of the ligands in the phosphorane.

Little is known about the existence of protonated phosphoranes. The formation of the protonated structure of a spirobicyclic phosphorane in the reversible acid catalysed hydroxyphosphorane–phosphate reaction (XLIII) ⇌ (XLIV) has been reported.[64] The study of the temperature variation of the ^1H, ^{13}C, and ^{31}P NMR spectra of certain monocyclic phosphoranes in the presence of small amounts of HSO_3F showed[158,159] that the protonated hydroxyphosphoranes are real intermediates in the reversible transition between dihydroxyphospholens and the isomeric enolphosphonium ions:



(10)

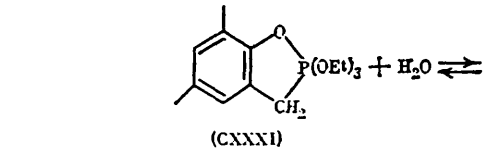
Table 4. Activation parameters for the phosphorane–dipolar ion equilibrium [Eqn.(10)].

Phosphorane	$\Delta H^{\neq}$, kcal mol^{-1}	$\Delta S^{\neq}$, e.u.	$\Delta G^{\neq}$, kcal mol^{-1}	Refs.
	2.8	−37	12.0	[159]
	3.0	−40	13.0	[160]
	2.6	−44	13.5	[160]

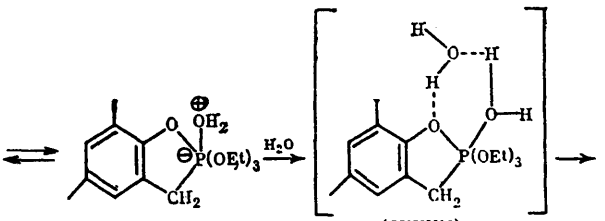
The rate of this process, which can be regarded as a model of intramolecular phosphorylation, is limited by structural factors and is entropy-controlled (Table 4). The equilibrium [Eqn.(10)] involves the bimolecular proton transfer between the protonated and neutral λ^5-1,3,2-dioxaphospholens. Equilibration is rapid when the ring contains a double bond and slow for saturated rings. It follows from the activation parameters for the phosphorane–phosphonium ion equilibrium[160,161] that the rigidity of the five-membered ring facilitates the ring closure to form the bicyclic phospholan structure, while in the case of a six-membered ring the process is less effective (Table 4).

The equilibria described here [Eqn.(10)] play an important role in the mechanism of the intramolecular phosphorylation of the 2-OH group in RNA, which is facilitated by the ribose ring.[160] It has also been noted that phosphorane–betaine interconversions of this kind are responsible for the ligand reorganisation processes involving spirocyclic arylphosphoranes, which are promoted by methyltrifluoromethanesulphonate.[162]

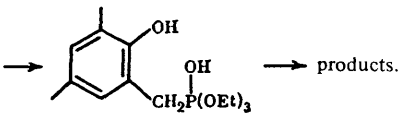
The associative mechanism has been demonstrated for the hydrolysis of the monocyclic phosphoranes (CXXXI) and (CXXXIII) in aqueous organic media.[163,164] The high values of the KIE (greater than 3), the large negative activation entropies, data concerning the influence of solvent polarity on the reaction rates, and the second (or higher) order of the reaction with respect to water suggest the formation of octahedral intermediates with phosphorus(VI). The subsequent involvement of a second water molecule in the process leads to ring opening products. The phosphorane (CXXXI) can form under these conditions the trimolecular complex (CXXXII):[163]



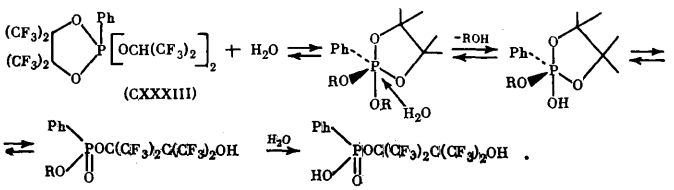
(CXXXI)



(CXXXII)



The hydrolysis of compound (CXXXIII) includes two pre-equilibrium stages—the formation of a hexacoordinate intermediate and exothermic opening of the λ^5-dioxaphospholan ring:[164]



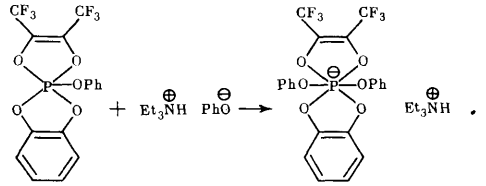
(CXXXIII)

The formation of intermediate hexacoordinate phosphorate anions in the base hydrolysis of phosphoranes is especially probable in the series of λ^5,1,3,2-diheterophospholans. This

has been confirmed by numerous examples of the isolation or identification in solutions of phosphorus(VI) anions[166–169] (see Sarma et al.[165] and the literature quoted therein).

It has also been suggested that hexacoordinate intermediates can arise in the hydrolysis of ethylene methyl phosphate in highly alkaline media.[170,171] However, recent NMR studies of this process failed to confirm such a possibility.[172]

The stereochemical relations in the process involving an increase of the coordination number [P(V) → P(VI)] are clearly demonstrated by the comparison of the molecular structures of the phosphorane (CXXXIV) and the phosphate anion (CXXXV) (Fig.3), formed as a result of the addition of the phenoxide ion to the phosphorus atom in compound (CXXXIV).[165] It is usually suggested that the attack by the nucleophile on the central atom takes place in the equatorial plane of the TBP:[167,173]



(CXXXIV) (CXXXV)

The approach of the phenoxide anion to the O(3) atom from the rear (Fig.3*a*) should lead to a "phosphorate" with the *trans*-disposition of the PhO groups; the *cis*-configuration is a result of the addition of PhO^- to O(2) and O(4) from the rear. It has been established[165] that the most favourable steric disposition of the ligands in the "phosphorate" (CXXXV) (Fig.3*b*) is obtained following the attack on O(4) from the rear in the last sbustituted region of the phosphorane (CXXXIV). The alternative attack on O(3) from the rear gives rise to the sterically less favourable "phosphorate".

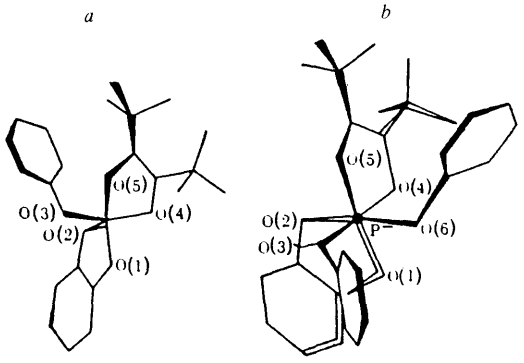


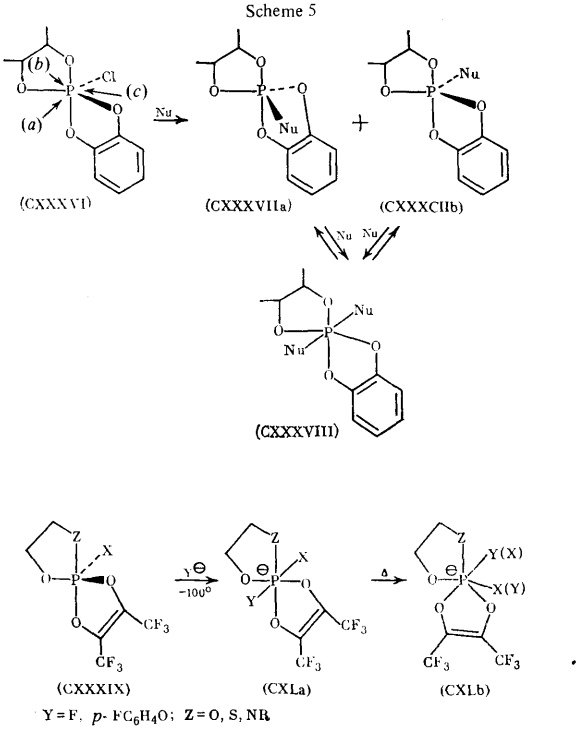
Figure 3. Molecular structures: *a*) phosphorane (CXXXIV); *b*) "phosphorate" (CXXXV).[165]

The stereochemical result of the $S_N2P(V)$ reactions depends to some extent on the nature of the nucleophile added to phosphorus(V) and on the leaving group.[173] The attack by the nucleophile on the phosphorus atom in exocyclic substitution reactions involving the phosphorane (CXXXVI) can proceed in principle via one of three pathways in the equatorial plane of the TBP (pathways *a*–*c*, Scheme 5). The *trans*-substitution via pathway *a* leads to the inversion of the configuration of the phosphorus atom, while *syn*-attack (pathways *b* and *c*) affords a product with retention of the configuration. Determination of the ratio of the stereoisomers (CXXXVIIa) and (CXXXVIIb) (7 : 1) by low-temperature ^{31}P NMR showed that the reactions of compound (CXXXVI) with dimethylamine and lithium dimethylamide proceed with the preferential inversion of configuration: $k_a = 7(k_b + k_c)$.

On substitution of PhO^- at −78 °C, the stereoisomeric composition corresponds to (CXXXVIIa) : (CXXXVIIb) = 1 : 1, while at room temperature the composition changes in favour of the isomer (CXXXVIIb) (0.64 : 1). Methyllithium gives rise to a mixture of equal amounts of the isomeric phosphoranes. The equilibration of the stereoisomers can be achieved via the hexacoordinate intermediate (CXXXVIII).

These results might have been interpreted on the assumption that the nucleophilic substitution at P(V) does not require the attack by the nucleophile of the leaving group.[173] However, it was later established for the interaction of phosphoranes of type (CXXXIX) with ionic nucleophiles at low temperatures (between −60° and −100 °C) that only the less stable *trans*-anions (CXLa), which isomerise to the "*cis*-phosphorates" (CXLb) on heating, are formed initially:

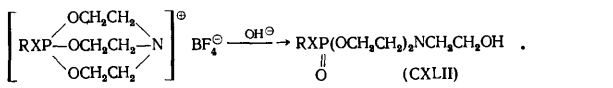
Scheme 5



The ease of the *trans*-attack, which is a kinetically controlled process, is due to the stereoelectronic effect of the LEP of the heteroatoms adjoining the P–Nu bond.[2,173] The *trans*-attack on spirocyclic phosphoranes of the type (CXXXIV) and (CXXXIX) is facilitated by the appropriate orientation of the LEP orbitals of the four heteroatoms, while the *cis*-attack is facilitated by only two of these orbitals.[174] The formation of the more stable *cis*-isomers (CXXXV) and (CXLb) is a thermodynamically controlled process, determined by the steric situation at the phosphorus(VI) atom [see the above remarks concerning the "phosphorate" (CXXXV)]. It has been noted[173] that the dissociative mechanism of the exocyclic nucleophilic substitution in spirocyclic phosphoranes is apparently impossible due

to the pronounced angular strain in the intermediate spirocyclic phosphonium cation. An analogous *cis–trans* isomerisation has been established also in a study of the interaction of the fluoride anion and the *p*-fluorophenoxide anion with λ^5-oxathia- and λ^5-oxaza-phospholens.[175]

As a consequence of the highly electrophilic properties of the phosphorus(V) atom, the attack by the nucleophile in the S_N 2P(V) processes is almost always directed at the phosphorus centre, in contrast to the nucleophilic substitution reactions at P(IV), where both the tetracoordinate phosphorus atom and the endo- or exo-cyclic carbon atoms can serve as centres for the nucleophilic interaction.[2] However, an instance of the selective pseudoequatorial attack by nucleophiles on the carbon atom in the TBP structure of the tricyclic phosphatranes (CXLI) has been observed recently:[176]



(CXLII)

The transannular N → P bond in these compounds ensures quinary coordination of the phosphorus atom. In all cases (X = O or S) the products of the alkaline hydrolysis are the phosphates (CXLII) and nucleophilic attack is directed selectively to the pseudoequatorial carbon atom. It is believed[176] that such interaction is a consequence of the internal properties of the electronic configuration of the TBP: as a consequence of the dative transfer of electron density from the pseudoequatorial oxygen atom to the phosphorus atom, in the initial structure there is already some predisposition towards the formation of the P=O π-bond, which arises as a result of the reaction. A deficiency of electron density is therefore produced at the pseudoequatorial carbon atom, which renders this centre most sensitive to nucleophilic attack.

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The data presented in this review demonstrate the multiplicity of the chemical properties of λ^5-1,3,2-diheterophosphacyclanes. The discovery of the role of cyclic phosphoranes and related structures with a phosphorus atom in the heterocycle (phosphonium cations, phosphoranide and hydroxyphosphoranide anions, "phosphorate" anions, and phosphorane–base complexes) as intermediates in many reactions of OPC, including those which have become classical, is of fundamental importance in this connection. This permits well-founded conclusions about the mechanisms of the reactions of OPC and indicates the usefulness of their investigation, particularly in relation to cyclic OPC. Various tautomeric processes and the relative ease with which the coordination number of the phosphorus atom can change in chemical reactions of OPC [P(III)–P(IV)–P(V)–P(VI)], which are particularly clearly manifested in the chemistry of cyclic phosphoranes, to a large extent predetermine the unity and wide variety in the phosphorus chemistry.

At the same time numerous questions concerning the reactivity of λ^5-1,3,2-diheterophosphacyclanes, such as the influence of the size of the heterocycle, of endocyclic heteroatoms, and of exocyclic functional groups and the quantitative estimation of the electronic and steric characteristics of phosphorus(V)-containing groups still await a more far reaching elucidation.

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The Electronic Structure and Reactivity of Palladium Compounds

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The state of the quantum-chemical theory of the electronic structure of palladium compounds has been examined. The results of quantum-chemical calculations for palladium(II) and palladium(0) compounds and palladium clusters, and also of calculations for model reactions of palladium compounds, have been discussed. Methods for analysing the relationship between the electronic structure and reactivity of palladium complexes have been examined.
The bibliography contains 121 references.

CONTENTS

I.	Introduction	1151
II.	General concepts	1152
III.	Quantum-chemical calculations of the electronic structure of palladium compounds	1153
IV.	Quantum-chemical studies of reactions involving palladium compounds	1158

I. INTRODUCTION

The high catalytic activity of metallic palladium in heterogeneous catalysis, for example the hydrogenation of unsatuarated compounds,[1] the catalytic reforming of petroleum,[2] and the conversion of carbon monoxide into methane or methanol,[3] is well known. Interest in the chemistry of palladium has been increasing since the late nineteen-fifties, when it was found that Pd^{II} complexes can oxidise alkenes selectively at low temperatures to give carbonyl compounds,[4,5] vinyl esters, acetals, and ketals.[6] These reactions not only provided a basis for industrial methods for obtaining acetaldehyde and vinyl acetate but also initiated the development of a new field in homogeneous metal-complex catalysis, based on the thermodynamic analysis of possible catalyst–substrate reactions and its use to construct a catalytic cycle.[7]

In the earliest papers by Syrkin and co-workers[5,6] it was suggested that the key compounds in the oxidation of alkenes by palladium complexes are organic derivatives of palladium with a metal–carbon σ-bond, produced by reactions of the initially formed alkene π-complexes of Pd^{II}. This suggestion, which at first appeared unusual and was not immediately accepted by organometallic chemists of the classical school, was subsequently proved by direct synthetic methods[7-9] and confirmed by kinetic studies.[9,10]

The chemistry of organic derivatives of palladium is now among the most well developed fields of the organic chemistry of transition metals.[11,12] It has become clear that the coordination possibilities of Pd compounds, their electronic structure, and their reactivity, which changes with change in the nature of the solvent and the ligands not taking direct part in the reaction, are most important factors which must be taken into account both in the analysis of the mechanism of the action of catalysts and in the prediction of their catalytic effect.

In the present review, the results of the quantum-chemical study of the electronic structure of palladium compounds are discussed. The main aims of the review are to compare the results obtained by different workers and by different

methods, to compare data on the electronic structure and properties of compounds of palladium and other elements of the platinum group, and to find methods for the quantum-chemical analysis of the relationship between the electronic structure of transition metal complexes and their reactivity.

II. GENERAL CONCEPTS

In the nature of the filling of its electron levels, the palladium atom occupies a unique position in the periodic system. Thus it is only for this atom in the ground state ^1S that the valence d-level is completely filled (electron configuration $4d^{10}$) while the outer 5s and 5p atomic orbitals (AO) are unoccupied. It should be noted for comparison that for the other elements of the platinum triad with ten valence electrons, the outer s-level is partly or completely filled: thus for platinum the ground state is the atomic state ^3D (configuration $5d^96s^1$), and for nickel ^3F (configuration $3d^84s^2$). As a result, the ionisation potential of the palladium atom $I_{Pd} = 8.33$ eV[13] corresponds to the ionisation of a 4d AO, whereas in the case of platinum the first ionisation potential $I_{Pt} = 9.0$ eV corresponds to the removal of an electron from the 6s AO. This characteristic feature of the electronic structure is related to the fact that in the Pd atom, the outer 5s and 5p AO have relatively high energies. Table 1 shows that the energies of electron promotion $d^{10} \rightarrow d^9s^1$ and $d^{10} \rightarrow d^9p^1$ increase considerably in the order Ni < Pt < Pd. At the same time, for palladium the outer 5s and 5p AO are much more extended in space (that is more diffuse) than its 4d AO. Thus the average radius of the Hartree–Fock 5s AO of palladium, equal to 0.194 nm for the state $d^9s^1(^3D)$, is more than twice the corresponding radius of the 4d AO (Ref.17, see Table 1), and much greater than the covalent radius of palladium (~0.13 nm).

Table 1. Ionisation potentials I, promotion energies E, and average radii R_d of the Hartree–Fock d AO of nickel, palladium, and platinum.

Atom	I, eV ($d^{10} \rightarrow d^9$)	E, eV		R_d, nm
		($d^{10} \rightarrow d^9s^1$)	($d^{10} \rightarrow d^9p^1$)	
Ni	5.81 [14]	−1.79 [15]	1.72 [16]	0.055 [17]
Pd	8.33 [14]	0.95 [15]	4.23 [13]	0.076 [17]
Pt	8.20 [14]	−0.76 [16]	3.28 [13]	—

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

Thus quantum-chemical calculations for palladium systems, in particular Pd^0 compounds, are of considerable interest, since the results reveal in purest form the role of the outer s and p orbitals of the transition metal in coordinate bond formation. Thus for example the ability of the Pd atom with its filled d level to undergo Pd ← L donor–acceptor interaction should be determined by the contribution of the unoccupied 5s and 5p AO to bond formation.

In the Ni–Pd–Pt series, the relative energetic and geometric characteristics of the valence d AO of palladium are characteristic of an element of the second transition series. With reference to energy, these orbitals are even more stable than the d AO of elements of the third transition series, whereas with respect to size they are still fairly highly localised.

Most published quantum-chemical studies have been devoted to calculations of the electronic structure of compounds of palladium in its typical formal oxidation states Pd^0 and Pd^{II}. The problem of determining the oxidation state in complexes of metals in low oxidation states is not simple. The formal oxidation state of a metal in a complex compound is defined as the charge produced on the given atom after the removal of the ligands. It is assumed that in the leaving carbon-containing ligands and acido-ligands (for example H^-, Cl^-, OH^-), the electron pair of the M–L bond remains associated with the ligand (that is the ligand is removed as an anion), and that molecular ligands are removed as uncharged species. In view of the variety of electronic characteristics of ligands, the classification of complexes according to the formal oxidation state of the metal is to a large extent arbitrary. The position becomes even more complicated when the ligands (for example the carbon atom in the system PdC examined in Refs.18 and 19) do not exist as free anions in solution.

One way of determining the oxidation state is by analysing the electron densities of the transition metal atom in a complex. Sometimes, the formal oxidation state is related to the effective charges of the atoms in the molecules, calculated by quantum-chemical methods. The charge of a transition metal atom, however, depends to a significant extent on the population of the outer s and p orbitals, and in the case of palladium an appreciable proportion of the electron density of these orbitals is localised outside the sphere of the covalent radius.[20] It seems more justified to relate the oxidation state not to the total charge of the palladium atom but to the total population of its valence d AO, which are localised mainly within the sphere of the covalent radius. If it is assumed that an increase in the oxidation state by one unit corresponds to an increase in the vacancy in the d level by 1 e, then the valence electron configuration of palladium is d^{10} for Pd^0, and d^8 for Pd^{II}.

To conclude this section, the quantum-chemical methods used in the calculations for the specific systems which will subsequently be examined can be considered. The different approaches were analysed in detail in Ref.21. For transition metal compounds, a reliable calculation of the bond strengths and the potential surfaces of reactions requires a non-empirical calculation using a large number of basis AO with subsequent allowance for the effects of electron correlation. A qualitatively reliable picture of the electron density distribution, and the relative energies of coordination for the simplest systems, can also be obtained, however, by non-empirical calculations by the SCF MO LCAO method using small basis sets requiring a much smaller volume of calculations. The volume of non-empirical calculations is often further reduced by using the valence approximation, in which the influence of the core electrons is effectively taken into account using atom pseudo-potentials.[22]

Since for most palladium systems the non-empirical level of calculation remains unattainable, simplified semi-empirical methods involving the complete neglect of differential overlap (CNDO)[23] and incomplete neglect of differential overlap (INDO),[24] and also the extended Hückel method (EHM),[25] are most frequently used. The approximations introduced in these methods lower the reliability of the quantitative results of the calculations. To decrease the error of the approximate methods, their parameters are calibrated using available experimental and theoretical data. The results of the calculations are analysed using different indices of

electronic structure, such as the Wiberg indices W_{AB}, the bond orders, and the two-centre components of the total energies E_{AB}.[26] Comparison of these indices makes it possible to study the regular features of the change in the electronic structure and reactivity in a series of related systems.

The SCF Xα scattered wave (SCF-Xα-SW) method[27] has also been used to study the electronic structure of Pd compounds. This method makes it possible to calculate satisfactorily the electronic spectra of transition metal compounds. At the same time, the approximations introduced in the SCF-Xα-SW method do not make it possible to calculate reliably the coordination energies and potential energy surfaces, and the specific form of representation of the wavefunction creates certain difficulties in the interpretation of the results of the calculations, in particular in the determination of the different indices of the electronic structure.

III. QUANTUM-CHEMICAL CALCULATIONS OF THE ELECTRONIC STRUCTURE OF PALLADIUM COMPOUNDS

1. The Electronic Structure of Pd^{II} Compounds

Typical palladium(II) compounds are square-planar complexes, for example K_2PdCl_4, and also the mixed complexes PdX_nY_{4-n} (where X represents an acido-ligand, Y a neutral donor ligand, and $n = 2$).[13] Calculations for the anionic complex $PdCl_4^{2-}$ have been carried out by the non-empirical SCF MO LCAO method,[28,29] the SCF-Xα-SW method,[30] and the semi-empirical INDO[31,32] and CNDO[33,34] methods.

The results of the calculations at first sight are inconsistent with the view that in the $PdCl_4^{2-}$ anion the oxidation state of palladium is +2. Thus according to the results of a non-empirical pseudo-potential calculation in the valence approximation in a minimum basis set[28] and INDO calculations,[31,32] the charge of the Pd atom is only 0.5e. If the total population of the 4*d* AO is considered, however, the electron distribution within the sphere of the covalent radius of the Pd atom is close to that expected for a Pd^{II} complex. The value obtained for the vacancy in the *d* level (~1.5e) is only 0.5e lower than that formally assigned to Pd^{II} (see section I).

As noted above, the low effective charge of Pd is due to the appreciable population of the diffuse outer 5*s* and 5*p* AO (their total population is close to 1e[31,32]). Their diffuse character is responsible for the appreciable contribution of these partly filled Pd orbitals to the Pd–Cl covalent bonding as a result of their extensive overlap with the orbitals of the Cl atom. Thus the overlap integrals of the 5*s* and $5p_x$ AO of palladium with the $3p_x$ AO of chlorine are $S(5s3p_x) = 0.23$ and $S(5p_x3p_x) = 0.32$, whereas $S(4d_{x^2-y^2}3p_x) = 0.10$.[32] Thus the outer 5*s* and 5*p* AO of palladium, together with the valence 4*d* AO, play an important part in the Pd^{II}–L bonding interaction.

Although expansion of the basis set in a non-empirical calculation for $PdCl_4^{2-}$ [28] has a marked influence on the effective charges of the atoms obtained by a Mulliken population analysis, the picture of the electron density distribution changes little, and the reported change in the effective charges is related to the arbitrary nature of the Mulliken procedure. Thus the negative charge of Pd, obtained in the non-empirical calculation in a two-exponent basis set,[28] is due to the assignment to the Pd atom of electron density associated with the polarisation *p* functions, which are much more diffuse than the 5*s* and 5*p* AO of palladium, corresponding to the bound atomic states. In fact, however, an appreciable proportion of this electron density should have been assigned to the ligands.

Thus to determine whether the charges obtained by semi-empirical methods are reasonable, they must be compared with the charges obtained by the non-empirical SCF MO LCAO method in a comparable minimum basis set. In this case the INDO parametrisation schemes[31,32] apparently give a reasonable electron distribution picture, whereas the CNDO parametrisation scheme[33] gives an unrealistic electron distribution.

Different methods give different relative distributions of the energies of the MO of the $PdCl_4^{2-}$ ion. Thus for the energies of the *d* levels (more accurately the energies of the MO consisting chiefly of the *d* AO of Pd), the following relationships have been obtained: $d_{x^2-y^2} > d_{xy} > d_{xz} \cong d_{yz} > d_{z^2}$,[30] $d_{x^2-y^2} > d_{xz} \cong d_{yz} > d_{xy} > d_{z^2}$,[32] and $d_{x^2-y^2} > d_{z^2} > d_{xz} \cong d_{yz} > d_{xy}$.[28,31]

The comparison of the results of calculations by the MO LCAO and Xα methods is somewhat arbitrary, since the energies of the MO have a different physical significance in these methods. The highest occupied MO were found to be those consisting chiefly of the *d* AO of the Pd atom in Ref.30, or the AO of the Cl atom in Refs.28, 31, and 32. The energies of the electron transitions were estimated in Refs.29 and 32 by independent SCF calculations for the ground and excited states; in Ref.34 by the SCF method with allowance for electron correlation within the framework of configuration interaction; and in Ref.30 by the transition state method.[27] The calculated energies of the lowest *d*–*d* transition and the lowest allowed charge-transfer transition L → Pd agree with the experimental data[35] in the case of the CNDO method.[34] This agreement may be accidental, however, since the energies of the subsequent *d*–*d* transitions show less satisfactory agreement with the experimental data.

The dependence of the electronic structure of square Pd^{II} complexes on the type of ligand has been studied.[33,36,37] CNDO calculations for the complexes PdX_4^{2-},[33] $PdX_3(C_2H_4)^-$ [36] (X = F, Cl, Br), and $Pd(PH_3)_2XY$ (X, Y = H, Cl, $OCOCH_3$, OH)[37] showed that in all cases the electron density on the Pd atom increases with decrease in the electronegativity of the ligands. For example, the effective charge of Pd calculated for the complexes *trans*-$XYPd(PH_3)_2$ increases from 0.51e for X, Y = H to 0.67e for X, Y = OR.[37] As in the case of $PdCl_4^{2-}$ examined above, the magnitude of the vacancy in the 4*d* level of Pd correlates with the formal oxidation state of palladium, that is in all cases it is close to 2e. An important role in the bonding interaction is played by the outer 5*s* and 5*p* AO of the Pd atom, which, in accordance with the calculated[37] covalent components of the Pd–L bond energy (E_{PdL}^{cov}), makes a significant contribution to the Pd–L covalent bonding. The observed increase in the charge of Pd with increase in the electronegativity of the ligands agrees with published data on the X-ray electron spectra[38–40] of Pd^{II} complexes.

A comparative estimation of the strength of the Pd–X bond in the complexes PdX_4^{2-} and the Pd^{IV} complexes PdX_6^{2-} showed[33] that the strength of the Pd–X bond increases with increase in the electronegativity of X and the coordination number of Pd. The regular features observed agree with conclusions[41] based on the experimental determination of the vibrational wavenumbers and force constants for the complexes $M_2[PdX_4]$ and $M_2[PdX_6]$.

The static *trans*-influence (and also *cis*-influence), revealed by the dependence of the strength of a palladium–ligand bond on the nature of the ligand in the *trans* (or *cis*) position, has been studied.[37,42,43] The stronger the *trans*

(or *cis*) influence of a ligand, the weaker the bond formed by its *trans* (or *cis*) partner in the square complex. Calculations have been carried out for the complexes $[PdCl_3L]^q$,[42] *trans*-$X_2Pd(NH_3)_2$ and *cis*-$X_2Pd(NH_3)_2$,[43] and *trans*-$XYPd(PH_3)_2$.[37] Series giving the order of the static influence of ligands have been constructed by analysing the two-centre components of the total energy E_{AB} and the Wiberg indices W_{AB}, which correlate with the strengths of the corresponding bonds.

The calculations for the complexes $[PdCl_3L]^q$ by the CNDO method[42] showed that the *trans*-influence of the ligand L decreases (and the strength of the Pd–Cl bond correspondingly increases) in the order $CN^- > CH_3^- > NO_2^- > H^- > Cl^- > SCH_3^- > NH_3 \cong CO \cong C_2H_4 > (CH_3)_2S > (CH_3)_2SO > H_2O$. Exactly the same series was obtained for the corresponding platinum complexes. From these and published data it was concluded that the position of a ligand in the order of the static *trans*-influence in palladium and platinum complexes is determined by its donor–acceptor properties; with increase in the donor power of the ligand, its *trans*-influence generally increases.

The calculations by the INDO method for the complexes *cis*-$PdX_2(NH_3)_2$[43] gave the following order of the *trans*-influence: $H^- > SCN^- > NCS^- > Cl^- > NH_3 > H_2O$. The *cis*-influence in the complexes *trans*-$PdX_2(NH_3)_2$ increases in the same order as the *trans*-influence in the corresponding *cis*-complexes, but the range of change in the values of E_{PdN}^{cov} with change in the nature of the *cis*-ligands is smaller by a factor of approximately 3.

The calculations for the complexes *trans*-$PdXY(PH_3)_2$ by the CNDO method[37] showed that for all ligands Y the *trans*-influence of X decreases in the order $X = H^- > Cl^- > OCOCH_3^- > OH^-$. The decrease in the *trans*-influence of the ligands in this series correlates with the increase in the negative charge on the ligand (more accurately on the atom of the ligand closest to palladium). This agrees with the published conclusion[42] that the *trans*-influence of a ligand increases with increase in its donor power. The hydride ligand, which shows the strongest *trans*-influence in the series studied, also forms the most covalent bond with palladium (judging from the values of the effective charges on X or from the Wiberg indices W_{PdX}). The highly covalent nature of the Pd–H bond is due to the lower electronegativity of H compared with other anionic ligands, and to the better ability of the 1*s* AO of the H atom to overlap with the diffuse 5*s* and 5*p* AO of the Pd atom.

The published quantum-chemical data on the *trans*-influence of the ligands in square Pd^{II} complexes[37,42,43] agree with one another. The *trans*-influence is revealed thermodynamically by the dependence of the instability constants k_{Cl} for the reaction

$$trans\text{-}[LMCl_3]^- + H_2O \rightleftharpoons [L(H_2O)MCl_2] + Cl^-$$

on the nature of L.

The order of the change in k_{Cl} agrees with the theoretical order of the *trans*-influence,[42] although the quantum-chemical calculation did not take account of the influence of solvation on this reaction. The conclusion that H has a strong *trans*-influence in Pd^{II} complexes is confirmed by the results of an X-ray diffraction study of the complex *trans*-$ClPd(H)(PPh_3)_2$, for which the bond length $R(Pd–Cl) = 0.247$ nm is much greater than the average value for Pd^{II} complexes, $R(Pd–Cl) = 0.223$ nm.[45] Thus the available experimental data confirm the regular features of the change in the *trans*-influence obtained theoretically.

A comparative study of the electronic structure of related complexes of Pd^{II}, Ni^{II}, and Pt^{II} has been carried out.[34,46–48] The complexes MCl_4^{2-}, $M_2Cl_6^{2-}$, $[MCl_3(C_2H_4)]^-$, and ML_2 with σ-donor ligands show an increase in the covalent character of the M–X bonds in the order Ni < Pd < Pt, revealed by a decrease in the effective charge of the central atom. A comparative non-empirical pseudo-potential calculation for the anion of Zeise's salt $[PtCl_3(C_2H_4)]^-$ and its palladium analogue[46] showed that on going from Pd to Pt the strength of the M–C_2H_4 bond increases: thus the calculated energy of the dissociation $[Cl_3M(C_2H_4)]^- \rightarrow [Cl_3M]^- + C_2H_4$ is 25 kcal mole^{-1} for Pt, and only 12 kcal mole^{-1} for Pd. In both cases the structures of $[Cl_3M(C_2H_4)]^-$ with ethylene arranged at right angles to the plane of the complex are energetically more favourable than those with the equatorial arrangement of the alkene molecule. The barrier to the rotation of ethylene about the M–C_2H_4 bond is low, and is to a large extent due to the increase in the C–Cl repulsion interaction on going to the planar structure. An estimate of the strength of the bonds in the complexes ML_2 by the CNDO method[48] also indicates that the strength of the M–L bond increases with increase in its covalent character in the order Ni < Pd < Pt. These results agree with the experimental estimation of the strengths of the M–C_2H_4 and M–L bonds in the complexes $[Cl_3M(C_2H_4)]^-$ and ML_2.[49]

The results are determined by the general regular features, noted above, in the change in the electronic structure of the transition elements, namely the increase in the diffuse character and simultaneous stabilisation of the valence *d* orbitals on going from the elements of the first transition series to the elements of the second and third series. The energy of interaction of orbitals *i* and *j* can be estimated in second-order perturbation theory using the expression[50]

$$E_{ij} = -\frac{H_{ij}}{\varepsilon_i - \varepsilon_j} \qquad (1)$$

where H_{ij} is the integral of the resonance interaction of the orbitals, which increases with increase in the degree of overlap of the orbitals, and ε_i and ε_j are the orbital energies. The more diffuse character of the 4*d* AO of the Pd atom and the 5*d* AO of the Pt atom compared with the 3*d* AO of the Ni atom is responsible for their greater overlap with the ligand orbitals, and hence for the higher value of E_{ij}. Moreover, for Pd and Pt, the lower-lying 4*d* and 5*d* AO are closer in energy to the ligand orbitals involved in the M–L bonds, compared with the 3*d* AO of the Ni atom. This also leads to an increase in E_{ij} as a consequence of the decrease in the difference $\varepsilon_i - \varepsilon_j$. Thus the electronic characteristics of the *nd* AO are responsible for the increase in the covalent bonding M–L in the order Ni < Pd < Pt.

The decrease in the polarity of the M–Cl bonds is also responsible for the observed[30,34] closer relative positions of the non-bonding levels of the M and Cl atoms for $PdCl_4^{2-}$ and $Pd_2Cl_6^{2-}$, compared with the corresponding Pt complexes. The highest occupied MO of the $PtCl_4^{2-}$ and $Pt_2Cl_6^{2-}$ ions consist chiefly of the *d* AO of the Pt atom, and lie appreciably higher than the other occupied MO. In the case of the Pd complexes, the relatively high effective charges of Pd and Cl stabilise the non-bonding MO consisting chiefly of the *d* AO of palladium, and destabilise the non-bonding MO localised on Cl (ϕ_{Cl}). This leads to the observed[30,34] approach of the energies of ϕ_{Cl} and the highest occupied molecular orbitals (HOMO) of the $PdCl_4^{2-}$ and $Pd_2Cl_6^{2-}$ ions.

This review of the results of quantum-chemical calculations for Pd^{II} complexes reveals the following regular features of their electronic structure: 1) the electronic characteristic correlating with the formal oxidation state of palladium in

Pd^{II} complexes is the magnitude of the vacancy in the valence 4*d* level of the Pd atom, which is close to 2e for the complexes for which calculations have been carried out; an important role in the Pd–L bonding interaction is played not only by the valence 4*d* AO but also by the outer 5*s* and 5*p* AO of palladium; 2) the electron density at the palladium atom decreases with increase in the electronegativity of the ligands; 3) the static *trans*-influence of the ligand generally increases with increase in its donor power; and 4) in a series of related compounds of Ni^{II}, Pd^{II}, and Pt^{II}, the strength of the M–L bonds increases with increase in their covalent character in the order Ni < Pd < Pt.

2. The Electronic Structure of Pd^0 and Pd^I Compounds

Compounds of zero-valent palladium (formal oxidation state 0) have been the subject of more non-empirical calculations than other palladium systems. The only Pd^I compound for which quantum-chemical studies have been carried out is apparently PdH.[17,18,51] The reason is probably that Pd^I compounds began to attract the attention of chemists only comparatively recently.[52–54] Calculations have been carried out[55] for the hydride complex of Pd^I $Pd_2(PH_3)_2H_2$. The study of the electronic structure of this complex, however, was not the aim of this work,[55] and its results will be discussed below (section V) in relation to the problem of the dissociative reaction of molecular hydrogen with palladium systems.

Following the principle formulated above, the oxidation state of palladium will be related to the magnitude of the vacancy in its valence *d* level. The data given in Table 2 show that, in agreement with the above conclusion, the magnitude of the *d* vacancy correlates with the formal oxidation state. Thus for the Pd^0 complexes $Pd(H_2)$, Pd(CO), and $Pd(C_2H_4)$, the electron configuration of the *d* AO is close to d^{10} (the values of the populations were not given for $Pd(C_2H_4)$, but the electron configuration of Pd is close to d^{10} [58,59]). On the other hand, for Pd^I hydride, the configuration of the *d* AO is close to d^9. It is also shown below that the magnitude of the *d* vacancy is one of the important electronic factors determining the relative strength of Pd–L bonds.

Comparison of the results of calculations for the PdCO, PdH, and PdC systems,[18] carried out in the same pseudopotential scheme, also makes it possible to estimate the oxidation state of Pd in palladium carbide. Table 2 shows that the magnitude of the *d* vacancy for palladium in PdC (~0.5e) is approximately equal to the average of the values for zero-valent palladium in PdCO and univalent palladium in PdH. Thus if the above criterion is applicable, the oxidation state of palladium in PdC is intermediate between 0 and +1. Unfortunately, there are no published data on the electron distribution in alkylpalladium systems, in particular for the important model system $PdCH_3$. It would also be of interest to estimate the change in the actual oxidation state of palladium in complexes with increase in its coordination number. In Refs.59 and 60–62, however, which give the results of non-empirical calculations for $Pd(C_2H_4)_n$ and $Pd(CO)_4$, no data are given on the population of the *d* AO of the Pd atom.

The formation of a *d* vacancy when the palladium atom is introduced into a complex may take place both as a result of Pd → L transfer of electron density and as a result of the promotion of electrons from the 4*d* to the 5*s* and 5*p* AO of palladium. In all the systems given in Table 2 except $Pd(H_2)$, the effective charge of Pd is positive as a result of Pd → L charge transfer. In the case of $Pd(H_2)$, the coordination of molecular hydrogen is determined chiefly by the donor–acceptor interaction of the filled σ-orbital (bonding orbital) of H_2 with the 5*s* and 5*p* AO of the Pd atom,[41] and the calculation in a minimum basis set gives a negative charge on the Pd atom. The positive charge of Pd, obtained in Ref.56 using two-exponent basis functions for H, is due to the population of the diffuse components of the 1*s* AO of the H atom. The assignment of a corresponding proportion of electron density to hydrogen is not completely justified, since the diffuse components of the 1*s* AO of the H atom overlap considerably the diffuse orbitals of the Pd atom, and their overlap density cannot be separated unambiguously.

Table 2. Results of non-empirical calculations for various simple model complexes of Pd^0 and Pd^I.

Compound	Z_{Pd}, e	Q_s, e	Q_p, e	Q_d, e	E_d, kJ mole^{-1}	Refs.
Pd (H_2)*	−0.08	0.24	0.12	9.72	23	[56]
Pd (H_2)	0.07	0.11	0.09	9.73	27	[56]
Pd (CO)	0.06	0.28	0.22	9.56	192	[57]
Pd (CO)	0.01	0.19	0.08	9.72	75	[18]
Pd (C_2H_4)	0.10	—	—	—	50	[58]
Pd (C_2H_4)	0.19	—	—	—	272	[59]
PdH	0.11	0.44	0.08	9.37	108	[18]
PdH	0.32	0.35	0.11	9.22	135	[17]
PdH	0.15	0.58	0.09	9.18	193	[54]
PdC	0.20	0.10	0.11	9.59	130	[18]
PdC	0.28	0.09	0.11	9.52	121	[19]

Notes: E_d is the dissociation energy, Z_{Pd} the effective charge on the Pd atom, and Q_s, Q_p, and Q_d the total populations of the valence 4*d*, 5*s*, and 5*p* AO of the Pd atom.

*For $Pd(H_2)$ the first row gives the results of the calculation in a minimum basis set, and the second row the results for an expanded basis set.

On going along the series of compounds PdL from L = H_2 to CO and C_2H_4 [56,57,59] there is a considerable increase in the dative transfer of electron density to the ligand, corresponding (in the Dewar–Chatt–Duncanson model) to the π-component of the Pd–L interaction. This is related to the fact that the unoccupied π*-orbitals of CO and C_2H_4, taking part in the dative interaction, have much lower energies than the antibonding orbital of H_2. Comparison of the results of non-empirical calculations for $Pd(H_2)$ [56] and PdCO,[57] carried out with allowance for all the electrons, shows that the increase in the dative interaction on going from $Pd(H_2)$ to PdCO is also accompanied by an increase in the donor–acceptor component, that is a synergic effect is observed. This leads to an appreciable increase in the strength of the bond, which for L = CO or C_2H_4 shows clearly defined covalent character. The observed increase in the strength of the Pd–L bond corresponds to the decrease in the total population of the 4*d* AO and the increase in the populations of the 5*s* and 5*p* AO of the Pd atom.

Overall, however, the total population of the 5*s* and 5*p* AO of palladium in Pd^0 and Pd^I compounds is much lower than 1e, that is the corresponding value for typical Pd^{II} complexes. This is due primarily to the fact that the ligands in the Pd^0 and Pd^I compounds are capable of donor–acceptor

interaction with the 5*s* and 5*p* AO to a much smaller extent than in the case of the anionic ligands of Pd^{II} complexes. In the Pd^0 and Pd^I compounds, the increase in the covalent contribution to the Pd–L bonding, accompanying the change to the electron configurations d^9s^1 or d^9p^1, does not compensate the expenditure of energy in the electron promotion $4d \rightarrow 5s$ or $4d \rightarrow 5p$. As a result, for a coordinate bond in these compounds, the optimum electron configuration of Pd is one in which the 5*s* and 5*p* AO have a low population.

Calculated data on the strength of the Pd–L bond Pd^0 and Pd^I compounds are contradictory, as can be seen, for example, by comparing the values given in Table 2 for the Pd–L (L = CO, C_2H_4) coordination energies obtained in different studies. It is of interest to compare the energies of different Pd–L bonds for which non-empirical calculations have been carried out in comparable and sufficiently large basis sets and in the same pseudo-potential scheme for PdCO, PdH, and PdC.[18] The increase in the *d* vacancy (chiefly in the $4d_\sigma$ AO oriented in the bond direction) on going from the zero-valent palladium compound PdCO to the univalent palladium compound PdH decreases the Fermi repulsion interaction between the electron of the $4d_\sigma$ AO of the Pd atom and the σ-orbitals of the ligands. This electronic factor is responsible for the greater strength of the Pd–H bond, compared with the Pd–CO bond.

The Pd–C bond in palladium carbide is even stronger than the Pd–H bond, although the magnitude of the *d* vacancy is smaller in the first case.[18,19] This is explained by the specific features of the electronic structure of the C atom acting as ligand. In the case of PdC, the σ-orbital of the carbide atom is unoccupied, and the only repulsion interaction of the Fermi type is the interaction of the electrons of the filled levels $d_\pi - \phi_\pi(C)$, which is much weaker than the corresponding interaction of the σ-orbitals. The resulting Pd–C bond is a single σ-bond. This bond, although stronger than the Pd–CO and Pd–H bonds, according to Ref.19 should be weaker than M–C multiple bonds, where M represents metals of neighbouring groups of the periodic system.

The $Pd...C_2H_4$ bond energy has been estimated[58,59] by a non-empirical calculation in the valence approximation using different pseudo-potential schemes. The value E_d = 50 kJ mole^{-1} was obtained for the dissociation energy of the $Pd...C_2H_4$ bond;[58] this shows qualitative agreement with infrared and ultraviolet spectroscopic data for this compound isolated in an inert matrix, which indicate the formation of a weak $Pd...C_2H_4$ bond.[63]

The high value obtained in Ref.59 for E_d for $Pd...C_2H_4$ (see Table 2) is apparently due to the overestimation (in the pseudo-potential scheme used[59]) of the contribution of the dative interaction of the 4*d* AO of palladium with the antibonding σ*-orbital of ethylene. The data in Ref.58, where a different scheme was used to construct the pseudo-potential, and also the results of a calculation for PdC_2H_4 by the SCF-Xα-SW method,[64] in agreement with qualitative perturbation theory, indicate that there is practically no interaction of the 4*d* AO of palladium with the high-lying σ*-orbital of C_2H_4.

A comparative study of the electronic structure of Pd^0 and Pd^I compounds in a series of related compounds of metals of the platinum group has been carried out.[17,47,64–66,51] In all the M^0 compounds for which calculations were carried out, as in the M^{II} complexes examined above, the effective charge of M decreases (the covalent character of the M–L bonds increases) in the order Ni, Pd, Pt. This is due to the fact that, as noted above, the d AO of the heavy metals (palladium and platinum) form more covalent bonds with the ligand orbitals, compared with the 3*d* AO of nickel.

This conclusion is confirmed by an analysis of the dative component of the M–L interaction in the π-complexes $M(C_2H_4)$[64] and $M(O_2)(PH_3)_2$.[66] In the complexes of both types, the bonding interaction of the filled d_π orbitals of the M atoms with χ_π ligand orbitals of appropriate symmetry increases in the order Ni < Pd < Pt. This conclusion was reached in Ref.64 from an analysis of the correlation diagrams of the one-electron levels, obtained by the SCF-Xα-SW method, and in Ref.66 by comparing the contributions of the dative interaction to the covalent component E_{M-O_2}, obtained by the CNDO method. In the last case it was shown that, in spite of the decrease in the transfer of electron density and going from Ni to Pt, the energy contribution of the dative interaction increases because of the increase in the overlap of the d_π and χ_π orbitals and the corresponding increase in the contribution of the covalent bonding M–L.

The large contribution of the dative interaction is responsible for the greater strength of the coordinate bond in the $Pd(C_2H_4)$ system compared with the isoelectronic system $[Ag(C_2H_4)]^+$.[59] In the case of $Pd(C_2H_4)$, the main contribution to the bond is made by the dative interaction of the $4d_\pi$ AO of palladium with the π*-orbital of ethylene, whereas in the case of $[Ag(C_2H_4)]^+$ it is made by the donor–acceptor interaction of the 5*s* and 5*p* AO of silver with the σ-orbital of ethylene, and the bond energy in the first case is 2.3 times that in the second.

In all the compounds studied, the estimated strength of the Pd–L bonds is lower than that of the corresponding Pt–L bonds, but in the case of $M(O_2)(PH_3)_2$, and also the hydrides MH,[17] the $Pd...O_2$ and Pd...H bonds are less stable than the $Ni...O_2$ and Ni...H bonds. Experimental data obtained for complexes with molecular nitrogen (in matrices)[67] and phosphine complexes[68,69] of zero-valent metals of the platinum group show that in these complexes Pd^0 again forms the weakest bonds.

Thus analysis of the quantum-chemical data indicates that the electronic factor preventing the formation of strong bonds in Pd^0 compounds is the relatively small magnitude of the *d* vacancy, which is related to the fact that the energy of electron promotion $nd \rightarrow (n+1)s$ or $nd \rightarrow (n+1)p$ has the highest value among the elements of the platinum group. With increase in the oxidation number, the magnitude of the *d* vacancy increases, but in the case of the hydride PdH it is again lower than the corresponding values for NiH and PtH, and the population of the 5*s* AO of palladium is lower that that of the 4*s* AO of nickel and the 6*s* AO of platinum. The Fermi repulsion interaction of the electrons of the filled $4d_\sigma$ AO of palladium and the σ-orbitals of the ligands decreases the strength of the Pd–L bond.

Calculations for Pd^0 complexes with a coordination number $n > 1$ were carried out not only in Ref.66 but also in Refs.62, 59, and 70. An interesting characteristic feature of Pd^0 and Pt^0 complexes is that, in addition to 18-electron complexes ML_4, low-coordinate 16-electron trigonal planar complexes ML_3 are also known. Examples of these complexes are provided by the complexes of palladium with tertiary phosphine ligands $Pd(PR_3)_3$ and the mixed phosphine complexes $PdX(PR_3)_2$ (X = alkene, O_2).[71,72] 14-electron complexes $Pd(PR_3)_2$ have also been obtained.[16] Experimental data indicate that the strength of the coordinate bond in Pd^0 complexes and the reactivity of these complexes depend on the coordination number of palladium.[16,73] The aim of the theoretical study is to determine the electronic factors which, in addition to steric factors, determine the optimum coordination number for Pd^0 complexes.

Comparative calculations for PdL_n complexes with different coordination numbers n[59,70] show (in agreement with experimental data) that the strength of the Pd–L coordinate bond decreases with increase in n. Thus a non-empirical pseudo-potential calculation for the complexes $Pd(C_2H_4)_n$ with $n = 1$, 3, and 4[59] showed that the coordination energy E_c corresponding to one ethylene molecule decreases on going from $n = 1$ to $n = 3$ and $n = 4$ by factors of 1.2 and 1.4 respectively. The marked decrease in the calculated values of E_c on going from $n = 1$ to $n = 4$ explains the fact that the coordination number of palladium in the compounds $Pd(C_2H_4)_n$ synthesised in inert matrices does not exceed 3.[63]

The electronic factors responsible for the decrease in the strength of Pd–L coordinate bonds when L is an electron σ-donor were established[70] by CNDO calculations for the model phosphine complexes $Pd(PH_3)_n$ ($n = 1$–4) and the hypothetical complexes $Pd(H_2)(PH_3)_n$ ($n = 1$–3). In this case a criterion of coordinative unsaturation of the complexes is provided by the relative energy of the lowest unoccupied MO (LUMO), localised on the transition metal atoms.[74] For phosphine complexes of Pd^0, these orbitals consist chiefly of the 5*s* and 5*p* AO of the Pd atom. Analysis of the results of the calculations[70] showed that the $L_nPd...H_2$ coordination energy and the strength of the individual Pd–L bonds decrease considerably with decrease in the valence angle L–Pd–L, or, which is the same thing, with change in the formal hybridisation of the 5*s* and 5*p* AO of palladium. The energy of the LUMO of the complexes PdL_n increases with increase in n, that is, as expected, the coordinative unsaturation of the complexes decreases with increase in the number of phosphine ligands.

The electronic factor responsible for the relative stability of the coordinatively unsaturated complexes PdL_n is the fact that the transfer of electron density to the 5*p* AO of the Pd atom becomes energetically unfavourable with increase in n.

Thus in the unsaturated 16-electron complexes PdL_3 and even in the 14-electron complexes PdL_2, the population of the high-lying 5*p* AO of palladium involved in bonding may reach a value such that its increase on the coordination of new ligands is energetically unfavourable. The optimum coordination number of the complexes of the platinum group metals is therefore determined not only by steric factors but also by electronic factors, in particular the relative arrangement of the *s*, *p*, and *d* levels of the M atom. This conclusion makes it possible to explain the observed difference in the coordination numbers of complexes of Ni^0, Pd^0, and Pt^0 with the same phosphine ligands, and also the difference in the coordination numbers for complexes ML_n with ligands having similar steric characteristics but different electronic characteristics.[16,73]

Analysis of the results of these quantum-chemical calculations of the electronic structure of Pd^0 and Pd^I compounds leads to some general conclusions. For Pd^0 and Pd^I compounds, as in the case of Pd^{II} compounds, the magnitude of the vacancy in the valence *d* level correlates with the formal oxidation state of palladium. The population of the outer 5*s* and 5*p* AO generally increases with increase in the *d* vacancy. The relatively small magnitude of the *d* vacancy is the electronic factor decreasing the strength of the Pd–L bonds in the Pd^0 compounds. The strength of the M–L bonds in compounds of a metal in a low oxidation state generally increases in the order Ni < Pd < Pt, if the main contribution to the bond is made by the dative component of the M–L interaction. When the donor–acceptor component of the M–L interaction is decisive, the strength of the Pd–L bond may be the lowest among the platinum group metals. The electronic factor responsible for the possible existence of coordinatively unsaturated Pd^0 complexes PdL_n (where L is an electron σ-donor and $n = 2$ or 3) is the fact that, with increase in n, the filling of the high-lying 5*p* AO of palladium, involved in the formation of the Pd–L bonds, becomes energetically unfavourable.

3. The Electronic Structure of Palladium Clusters

In the present section, the results of the quantum-chemical study of atomic clusters Pd_n ($n = 2$–79)[51,75–85] and the few calculations for polynuclear complexes Pd_mL_n[34,86,87] are discussed. The experimental and theoretical study of clusters is an important independent field.[88] At the same time, quantum-chemical calculations for clusters, in particular palladium clusters, are also of interest for the theory of catalysis, particularly heterogeneous catalysts, in relation to the problem of studying the electronic structure and properties of catalytic systems. The cluster model makes it possible to obtain valuable information on the electronic nature of the Pd–Pd bond, and also on the dependence of the properties of the system on the number of Pd atoms.

A key cluster system is the simplest cluster Pd_2, for which experimental spectroscopic data are available.[89,90] The main aim of the quantum-chemical studies carried out in Refs.51 and 75 was the estimation of the strength of the bonds formed by two palladium atoms with filled *d* levels. The calculations for Pd_2 were carried out by the non-empirical SCF MO LCAO method[75] and also by the two-configuration SCF method,[51] in the valence approximation. A pseudo-potential non-empirical calculation has also been carried out for the cluster Pd_3.[75] A number of calculations for the clusters Pd_5, Pd_6, and Pd_{13}, and also a study of the adsorption of atomic oxygen and CO on Pd_5 clusters and of atomic hydrogen on Pd_6 clusters, have been carried out by the SCF-Xα-SW method.[76–78] The other cluster calculations[79–87] were carried out in the CNDO approximation, and also by the EHM.

The results of the calculations for Pd_2 carried out by different methods are contradictory. Thus the calculation by the two-configuration SCF method[51] gives the dissociation energy value $E_d = 72.3$ kJ mole^{-1}, in satisfactory agreement with the spectroscopic estimate of 63 ± 19 kJ mole^{-1}.[90] On the other hand, a non-empirical SCF MO LCAO calculation[75] in a minimum basis set with the addition of polarisation *d* functions gave a bond energy value close to zero. A calculation in a basis set selected according to the "counterbalance" scheme,[91] that is using a complete molecular basis set in the calculation for individual palladium atoms, gave a potential curve of the repulsion type. In Ref.75, a calculation for the cluster Pd_3 was carried out using the same basis set as for Pd_2, and, as in the case of Pd_2, it was concluded that no bond is formed. The standard choice of basis set and the use of the "counterbalance" scheme give the same value of E_d for Pd_3. The most stable Pd_3 structure examined was the linear structure.[75]

A possible reason for the lack of agreement in the results in Refs.51 and 75 may be that in Ref.75 the effects of Coulombic correlation, which are particularly important for transition metal clusters,[92] were not taken into account.

According to the results of non-empirical calculations[51,75] and CNDO and EHM calculations,[79–81] the bond between palladium atoms with a filled 4*d* level is due chiefly to the participation of the unoccupied 5*s* AO of the Pd atoms in the bonding interaction. According to Refs.75 and 79, palladium in Pd_2 has a valence electron configuration close to d^{10}. On the other hand, the electron configuration

calculated in Refs.51 and 81 is close to d^9s^1. This difference is undoubtedly due to the characteristic features of the calculation methods used.

A comparison[82] of the results of calculations for the clusters Pd_{13} and Pd_{19} by the standard EHM and the version self-consistent with respect to charges and configurations showed that the first method gives an insufficiently reliable picture of the electron density distribution. In the standard version, in particular, the total population of the 4*d* AO of palladium is lowered considerably, and this may be the reason for the electron configuration d^9s^1 obtained for Pd_2 in Ref.81. In the case of the non-empirical calculation,[51] the use of the atom pseudo-potential to take effective account of the interaction of the valence and core electrons gives an incorrect (compared with the experimental estimate[15]) difference in the energies of the configurations d^{10} and d^9s^1, and this may influence the calculated values of the population of the 5*s* AO. To obtain more reliable information on the electron configuration of Pd in Pd_2 it is apparently necessary to carry out a more rigorous non-empirical calculation with allowance for all the electrons, and also with allowance for the effects of Coulombic correlation.

Thus even for the simplest palladium cluster, the data on the nature of the Pd–Pd bond are still unreliable. With allowance for this, the analysis of the results of calculations for more complex clusters can be carried out primarily on the basis of qualitative conclusions about the regular features of the change in the electron characteristics in a series of related systems. Calculations for clusters larger than Pd_2 have been carried out by the EHM,[82–85] and Pd_{13} has also been studied by the SCF-Xα-SW method.[76]

In Ref.76 it was found that an appreciable charge accumulates on the central Pd atom in Pd_{13}. The orbitals localised on the outer atoms are mainly the HOMO, many of which are non-bonding. In turn, a low-lying bonding MO with an appreciable contribution from the 5*s* AO of palladium is localised chiefly on the central Pd atom. These results show qualitative agreement with the results of a calculation for the cluster Pd_{19}, self-consistent with respect to charges and configurations, carried out by the EHM.[83]

The adsorption of atomic hydrogen on Pd clusters was studied in Refs.77, 79, and 85, and the adsorption of atomic oxygen and CO on Pd_5 was studied in Ref.78 (the calculations for the reaction of H_2 with Pd_2 and Pd_9 clusters, carried out in Ref.85, will be discussed in section IV). For all the clusters, an appreciable contribution to the Pd–L bond is made by the 5*s* and 5*p* AO of palladium. Thus in the octahedral cluster Pd_6H, according to the results of a calculation by the SCF-Xα-SW method,[77] the contribution of the 5*s* and 5*p* AO of palladium to the MO corresponding to the Pd–H bond is 76% of the contribution of the *d* AO.

In Ref.78, the same method was used to carry out a calculation for two structures of $Pd_5(O)$ modelling two possible versions of the coordination of O on a metallic palladium surface. In the first structure, the O atom is coordinated to the central Pd atom of a Pd_5 cluster (all the Pd atoms lie in the same plane). In the second structure, four Pd atoms lie in same plane, and the O atom and the fifth Pd atom lie on the principal axis of Pd_4, on different sides of this plane. The calculated spectra and the experimental infrared spectra for the adsorption of atomic oxygen on metallic palladium were compared. It was concluded that the single-point adsorption of O corresponds to the experimentally observed form of adsorption with a weak O–M bond, and that the many-point adsorption corresponds to the form of adsorption with a relatively strong O–M bond.

The electronic structure of dinuclear palladium complexes has been studied.[34,86,87] In Ref.87, calculations were carried out for the linear systems formed by the Pd^0 phosphine complexes $Pd_2(PH_3)_2$ and $Pd_2(PPhH_2)_2$, and also for a number of structures $Pd_2(PPhH_2)_2$, modelling the intramolecular coordination Pd...P in the dinuclear complexes $Pd_2(PPh_3)_2$.[93,94] The results of the population analysis indicate that a weak Pd–Pd bond is formed. This bond, in agreement with the results obtained for the dinuclear clusters Pd_2, can be described as a σ-bond produced mainly by the interaction of the $4d_{z^2}$ AO of one Pd atom and the 5*s* AO of the other Pd atom.

As noted in Ref.87, the formation of a Pd–Pd multiple bond might have been expected for the linear structures. Thus in terms of the concept of isolobality developed by Hoffmann,[95] if the difference in the filling of the orbitals are ignored, the fragment PdL, which has boundary sp_z, p_x, and p_y orbitals, can be compared with a CH group. As shown by the analysis in Ref.87, however, Pd–Pd multiple bonds involving *spd* hybrid orbitals are not formed, since electron promotion for the 4*d* to the high-lying 5*p* AO is energetically unfavourable.

The unoccupied 5*p* AO of palladium in Pd_2L_2 can take part in additional interactions. Thus the bonding donor–acceptor interaction of the 5*p* AO of a Pd atom with a phenylphosphine ligand of a neighbouring Pd atom (more accurately with the filled π-orbital of the aromatic ring) leads to additional stabilisation of the complex Pd_2L_2 and is possibly the reason for the observed stability of the coordinatively unsaturated complexes $Pd_2(PPh_3)_2$.[87]

In dinuclear and polynuclear Pd^{II} compounds, the distance between the palladium atoms is usually appreciably greater than the sum of their covalent radii. The electronic structure of the complex of palladium with dithioacetic acid $Pd_2(CH_3CSS)_4$, which has a short Pd–Pd bond and in which all four dithioacetate ligands occupy bridging positions, has been studied.[86] It is of interest to compare the results obtained with the results of a calculation[34] for the complex $Pd_2Cl_6^{2-}$ with two bridging ligands, where it is known that there is no direct Pd–Pd interaction. According to Refs.34 and 86, the absolute magnitude of the effective charge of the bridging ligands Cl and CH_3CSS ($Z_{Cl} = -0.41e$, $Z_{CH_3CSS} = -0.50e$) is smaller than that of the corresponding values $Z_{Cl} = -0.60e$ and $Z_{CH_3CSS} = -0.53e$ for the terminal Cl atoms in $Pd_2Cl_6^{2-}$ and the ligands CH_3CSS in the mononuclear complex $Pd(CH_3CSS)_2$. The Pd–Pd bond in $Pd_2(CH_3CSS)_4$ is a weak σ-bond. In Ref.34 it was noted that it is important to take account of configuration interaction in the calculation of the electronic spectra of $Pd_2Cl_6^{2-}$. Allowance for this factor leads to a marked displacement of the bands in the calculated spectra of $Pd_2Cl_6^{2-}$ to longer wavelengths compared with $PdCl_4^{2-}$, and to better agreement with the experimental data.[96–98]

IV. THE QUANTUM-CHEMICAL STUDY OF REACTIONS INVOLVING PALLADIUM COMPOUNDS

The results of the quantum-chemical study of the key elementary stages of processes catalysed by palladium complexes, or reactions responsible for the production of the catalyst, will be examined. The quantum-chemical mechanisms of the most important reactions of palladium compounds, namely the reaction of Pd^{II} and Pd^0 complexes with molecular hydrogen, the hydroxopalladation of alkenes, and various other reactions, have been studied.[55,56,79,85,99–105] The first non-empirical calculations in this field were carried

out in studies of the reaction of molecular hydrogen[56] and methane[99] with a palladium atom, and also the calculation for the model reaction of the insertion of CO into the Pd–H bond in the $[HPdCO]^+$ system.[100] The other calculations were carried out by the CNDO method using the parametrisation schemes proposed in Refs.36 and 37, and also by the EHM.

1. The Study of the Reaction of Molecular Hydrogen with Palladium Compounds

An important preparatory stage in catalytic processes involving the reactions of molecular hydrogen is the coordination of H_2 to a transition metal atom. In all published quantum-chemical studies of the activation of H_2 by the reaction with palladium compounds,[55,56,79,85,101,102] the initial systems examined contained H_2 coordinated in the molecular form to a Pd atom or (in polynuclear systems) at a Pd–Pd bond.

The calculations show that molecular hydrogen can be coordinated as an isolated ligand. The results of a complete non-empirical calculation for the simplest system $Pd(H_2)$,[56] partly discussed above are of particular interest. According to Ref.56, the Pd...H_2 interaction gives a complex containing bound (albeit weakly) molecular hydrogen. Thus the calculation in the largest of the basis sets used in Ref.56 for a fixed H–H bond length (R(H–H) = 0.074 nm) gives for the optimum T-shaped structure with R(Pd–H) = 0.2 nm a bond energy of E_d = 27 kJ mole^{-1}. As noted above, the coordination of H_2 involves chiefly a donor–acceptor interaction with the outer 5*s* and 5*p* AO of the Pd atom. The results of Ref.56 led to the general suggestion that transition metals can form stable complexes with molecular hydrogen as an isolated ligand. The theory of this type of coordinate bond was developed in Ref.106. A recent report[107] of the direct structural identification of tungsten and molybdenum complexes with molecular hydrogen confirmed this suggestion.

The activation of molecular hydrogen in a catalytic process involving transition metals leads finally to the rupture of the H–H bond. Both homolytic and heterolytic rupture of the H–H bond can be expected, depending on the nature of the transition metal, its oxidation state, and the nature of the coordinated ligands. The role of the electronic factors determining the mechanism of the activation of H_2 in its reaction with palladium compounds has been studied.[55,79,85,101,102] In Ref.101, a CNDO calculation was carried out for the heterolytic rupture of the H–H bond by a dissociative replacement mechanism in the reaction of H_2 with Pd^{II} complexes. In the other works cited, the homolytic rupture of the H–H bond in the reaction of H_2 with Pd^0 compounds was modelled.

The heterolytic rupture of the H–H bond is regarded as the initial stage in the selective catalytic hydrogenation of unsaturated compounds.[93,108–110] The starting materials in this reaction are mixed Pd^{II} complexes PdX_2L, where L is phosphine ligand. An interesting feature of this reaction is that the complexes PdX_2L_2 with oxygen-containing ligands X show a much higher activity towards H_2 than the corresponding complexes with halide ligands. From an analysis of experimental data, a four-centre mechanism was proposed for this reaction,[109,110] according to which the central atom captures a hydride ion, while the coordinated anionic ligand facilitates the capture by accepting the proton liberated:

$$PdX_2L_2 + H_2 \rightarrow (H)XPdL_2 + HX$$

The process is controlled by the interaction of the orbitals which are involved to the greatest extent in the bonds which are being formed or being broken in the dissociative replacement. These orbitals are the 1*s* AO of the H atoms, the localised hybrid orbitals of the Pd and X atoms, taking part in the Pd–X bonds, and the orbital of the unshared pair of the ligand X. In the state in which the H_2 molecule occupies a vacant coordination position in the original complex, the highest occupied MO are the MO of the unshared pair of X and the MO which corresponds to the antibonding combination of the bonding orbitals of the H–H and Pd–X bonds. The lowest unoccupied MO is the bonding combination of the antibonding orbitals of the H–H and Pd–X bonds. In the final state, the highest occupied MO will be the orbital of the unshared pair of X, formed as a result of the rupture of the Pd–X bond, and the MO which corresponds to the antibonding combination of the bonding orbitals of the Pd–H and H–X bond. The lowest unoccupied MO will be the bonding combination of the antibonding orbitals of the Pd–H and H–X bonds.

The intermediate cyclic state of the system can be examined by analogy with a five-orbital system of the polyene type,[111] if it is assumed that the ends of the chain are the orbitals of the anionic ligand X, not interacting with one another. The correlation diagram for this process differs from the familiar diagram[112] for the symmetry-forbidden redistribution of the bonds in the four-centre four-electron system

$$X{-}X' + Y{-}Y' \rightarrow XY + X'Y'$$

only in the presence of the unshared pair of the anionic ligand X. This difference, however, may lead to significant differences in the energies of these two processes. The non-bonding orbital of the unshared electron pair of the ligand X correlates with the practically non-bonding HOMO of the intermediate state, so that the dissociative replacement, generally speaking, is not symmetry-forbidden.

The initial stage of this process was modelled in Ref.101. The calculation was carried out after selecting structures describing the coordination of H_2 in the unoccupied coordination position of square complexes $PdX_2(PH_3)_2$, where X = Cl, OH, $OCOCH_3$, and also structures in which the coordinated H_2 molecule was displaced towards the anionic acido-ligand.

The calculations show that one of the electronic factors responsible for the heterolysis of H_2 is the donor–acceptor interaction of the filled σ-orbital of H_2 (the bonding combination of the 1*s* AO of hydrogen) with the unoccupied 5*sp* hybrid orbital. The rehybridisation of this orbital when H_2 is displaced towards the acido-ligand X ensures a bonding Pd...H_2 interaction when H_2 approaches X in all the structures examined. This bonding interaction facilitates the heterolysis. The donor–acceptor transfer of electron density $\sigma(H_2) \rightarrow 5sp$(Pd) to the H atoms produces a positive charge, which is responsible for the direct reaction of the coordinated H_2 molecule with the anionic acido-ligand X. This interaction leads finally to the heterolytic rupture of the H–H bond.

The rupture of the H–H bond corresponds to the filling of the σ^*-orbital of H_2 (antibonding combination of the 1*s* AO of hydrogen). In the case of dissociative replacement by a four-centre mechanism being considered, the metal-complex system does not have a high symmetry, and the filling of $\sigma^*(H_2)$ involves the mixing of the LUMO of the original structure, which contains a contribution from $\sigma^*(H_2)$, with the orbital of the unshared pair of the ligand X and the occupied MO containing a contribution from the bonding σ-orbital of H_2. The resulting HOMO of the

transition state has a node at the H atom closest to the anionic ligand, and describes the polarisation of the coordinated H_2 molecule.

The electronic factors stabilising the HOMO of the intermediate state should also stabilise the intermediate state as a whole, that is it should lower the activation barrier of the reaction. In the case being considered, where the HOMO has an electron density deficit at the H atom closest to X, this electronic factor is the Coulombic attraction $H^{\delta+}...X^{\delta-}$. The calculation in Ref.101 indicates that there is appreciable direct interaction between the coordinated H_2 molecule and the oxygen-containing anionic ligands OH and $OCOCH_3$, to which the main contribution is made by the Coulombic attraction $H^{\delta+}...OR^{\delta-}$.

Analysis of the two-centre components E_{HX} and the relative energies of the structures modelling the displacement of H_2 towards X shows[101] that the heterolytic rupture of the H–H bond should be easier for complexes with oxygen-containing ligands than for chloride complexes. This is because the ligand OR has a greater affinity for the H atom carrying the positive charge. Greater basic strength in X should also facilitate the stabilisation of the final state, making the formation of HX energetically more favourable. The results of the calculations in Ref.101 make it possible to explain the available experimental data and confirm the four-centre mechanism, proposed[109,110] on the basis of these data, for the heterolytic rupture of the H–H bond in the reaction with Pd^{II} complexes.

In the reaction of molecular hydrogen with Pd^0 compounds, the activation of H_2 takes place by a different mechanism, namely the oxidative addition of H_2 with the homolytic rupture of the H–H bond:

$$M_n + H_2 \rightarrow \begin{matrix} H \\ \diagdown \\ \diagup \\ H \end{matrix} M_n$$

For example, the dissociative chemisorption of H_2 on metallic palladium takes place by the oxidative addition mechanism.[113] This mechanism was studied by quantum-chemical methods in Refs.79, 85, and 102. In Ref.102, the complete non-empirical SCF MO LCAO method in a minimum basis set was used to carry out a calculation for the dissociation of H_2 in the coordination sphere of a Pd atom. In Ref.79, the CNDO method was used to study the reaction of H_2 with a Pd_2 cluster, and in Ref.85 a calculation was carried out for the Pd_9H system by the EHM. In addition, in Ref.55, the CNDO method and the parametrisation scheme used in Ref.79 were used to carry out a comparative calculation for the reaction of H_2 with mononuclear phosphine complexes of Pd^0 and Pt^0 of the type ML_2, and also with a dinuclear complex Pd_2L_2.

In Ref.102, the dissociation of H_2 in the $Pd(H_2)$ system was modelled by increasing the H–Pd–H angle (α) for a fixed bond length R(Pd–H) = 0.17 nm, since the optimum Pd–H bond length was found to be close to 0.17 nm both for the original complex with molecular hydrogen (α = 25°) and for the final linear dihydride structure.

With increase in the angle α, the population of the 5*s* and 5*p* AO of the Pd atom increases sharply, and in the case of angular structures with $\alpha \cong 90–148°$ the valence electron configuration of the Pd atom becomes close to d^9s^1. With further increase in α, the symmetry of the Pd orbitals involved in the H–Pd–H interaction changes. This leads to inversion of the populations of the boundary orbitals; the highest occupied MO is then the orbital corresponding to the interaction of the $5p_z$ AO of the Pd atom with the σ^*-orbital of H_2, and the valence electron configuration of Pd becomes close to d^9p^1.[102]

It was found that the formation of the dihydride is energetically unfavourable. This is due to the fact that the covalent bonding of the 1*s* AO of hydrogen with the hybrid *sp* (for $\alpha < 148°$) and *pd* (for $\alpha > 148°$) orbitals of Pd does not compensate the expenditure of energy in the electron promotion from the 4*d* AO to the high-lying 5*s* and 5*p* AO of the Pd atom. As a result, the molecular complex (α = 25°) is most stable. The angular structure undergoes an activationless transformation into the molecular complex The linear structure has a higher energy than the angular structure, but there is an energy barrier between them, associated with the rearrangement of the electron configuration $d^9s^1–d^9p^1$. It follows from the results in Ref.102 that for a metal such as palladium, the dissociation of hydrogen on a single centre is impossible, since it involves the promotion of an appreciable electronic charge to the high-lying 5*s* and 5*p* AO of palladium.

In Ref.79, where a CNDO calculation was carried out for the Pd_2H_2 system, it was again concluded that the dissociation of H_2 to give terminal hydride bonds Pd–H is energetically unfavourable. The molecular complex in which the H_2 molecule, coordinated in a bridging position, is arranged symmetrically and perpendicular to the Pd–Pd axis, is most stable. The structures Pd–Pd–H_2 with single-point coordination of H_2 are less stable, but all the structures with H_2 in the molecular form are more stable than the linear and rectangular dihydride structures.[79]

The conclusion[56,79,101] regarding the relative stability of the molecular coordination of H_2 in its single-point and two-point interaction with Pd atoms agrees qualitatively with the results of an experimental study of the chemisorption of H_2 on the surface of palladium black.[113] In this study[113] pulse volatilisation under super-high vacuum conditions ($\sim 5 \times 10^{-9}$ mmHg) detected four different states of chemisorbed H_2 on the palladium surface. The study of the physical characteristics of these states indicated that the state which is formed at a temperature below 100 K and which is desorbed at 250 K with an activation energy of 54–58 kJ $mole^{-1}$ probably corresponds to the molecular state of chemisorbed hydrogen. According to Ref.113, this molecular state may play the role of intermediate in the absorption of molecular hydrogen by metallic palladium.

The EHM has been used[85] to study the dissociative chemisorption of H_2 in the model cluster system $Pd_9–H_2$. In this case the dissociation of H_2 is energetically favourable.

The picture of the dissociative interaction of H_2 with one and with two Pd atoms obtained in Refs.79 and 102 shows complete agreement with the results of the comparative calculation[55] by the CNDO method for the interaction of H_2 with mononuclear phosphine complexes of Pd^0 and Pt^0 of the type $M(PH_3)_n$ and the dinuclear complex $Pd_2(PH_3)_2$. The latter models the complex $Pd_2(PPh_3)_2$ formed by the reduction of the compound $[(Ph_3P)Pd(OAc)_2]$ by molecular hydrogen.[93,94] $Pd_2(PPh_3)_2$ reacts with H_2 and palladium (II) complexes to form the polynuclear complexes $[(PhP)_2Pd_5]_n$ responsible for the catalysis.

Comparative calculations for mononuclear complexes of Pd^0 and Pt^0 and also dinuclear Pd^0 complexes, are of interest, since these complexes show different reactivities towards H_2. Thus mononuclear phosphine complexes PdL_n, where L is a phosphine ligand, do not react with molecular hydrogen,[71,73] the dinuclear complex $Pd_2(PPh_3)_2$ adds on H_2 easily and reversibly,[93,94] and the Pt^0 complexes PtL_2 undergo dissociative addition of hydrogen under mild conditions to give dihydride complexes of Pt^{II}.[73]

The change from mononuclear Pd complexes to the dinuclear complex corresponds to an increase in both the stability of the molecular complexes $L_nPd_m(H_2)$ with respect to

dissociation to L_nPd_m and H_2 and the relative stability of the dihydride structure HPd_mL_nH compared with the corresponding molecular complex $L_nPd_m(H_2)$. The explanation is that the formation of multicentre bonds Pd...H_2...Pd in the molecular complex and of multicentre hydride bonds Pd–H–Pd with the same strength as the corresponding bonds in the mononuclear complexes requires a smaller total transfer of electronic charge from the 4*d* to the 5*s* and 5*p* AO of palladium. In all the hydride structures, the population of the 5*s* and 5*p* AO is much greater than in the corresponding complexes with the H_2 molecule, and the hydride H atoms carry a negative charge.[55]

The dissociative addition of H_2 to the dinuclear complex Pd_2L_2 is energetically unfavourable, although to a smaller extent than the dissociative addition of H_2 to the mononuclear complexes PdL_n. The highest stability corresponds to the dinuclear structure in which the hydrogen molecule is arranged symmetrically and at right angles to the Pd–Pd bond. In the case of dinuclear structures in which H_2 is coordinated to one palladium atom, the $H_2...Pd_m$ coordination energy is lower and almost the same as for the mononuclear complexes. For reaction with two Pd atoms, the coordination energy of H_2 increases additively, and this is responsible for the additive character of the outer slightly filled 5*s* and 5*p* AO of the Pd atom with the σ-orbital of H_2.[55]

The platinum complexes have a greater ability to undergo the dissociative addition of H_2, compared with the palladium complexes.[55] This difference is due to the fact that the transitions $d \rightarrow s$ and $d \rightarrow p$ take place more readily in the case of platinum.

The above results[55] make it possible to explain experimental data on the difference in the reactivities of mononuclear and dinuclear Pd^0 complexes, and also Pt^0 complexes, with respect to molecular hydrogen. A comparison of calculated and experimental data[55] indicated that the compound formed by the reaction of $Pd_2(PPh_3)_2$ with H_2 is apparently the first example of a complex with H_2 in the molecular form. As noted above, similar complexes were recently identified for tungsten and molybdenum.[107]

These calculation results show the role of the outer *s* and *p* orbitals of the transition metal in oxidative addition. In the case of Pd^0 compounds, the oxidative addition of H_2 to one or two palladium atoms is energetically unfavourable because the formation of "normal" covalent bonds Pd–H involves considerable expenditure of energy to give the Pd atom a valence electron configuration close to d^9s^1. It may be assumed that with increase in the number of palladium atoms reacting directly with H_2, the strength of the $Pd_m...H_2$ bond will increase (both for structures with molecular H_2 and for dihydride structures), just as it increases, according to calculations,[55] on going from mononuclear to dinuclear systems.

Thus the dissociative chemisorption of molecular hydrogen on a metal is due to the multicentre interactions of the H atoms of the dissociating molecule with several metal atoms on the surface. According to Refs.55 and 114, a possible mechanism for the dissociative chemisorption of H_2 in its reaction with polynuclear palladium systems involves the initial adsorption of the H_2 molecule on a Pd atom or a Pd–Pd bond, after which the H atoms move apart into neighbouring interstices. The stabilisation of the resulting hydride structures takes place as a result of the increase in the number of metal atoms with which the hydrogen atoms interact.

The principal results of quantum-chemical studies of the reaction of molecular hydrogen with Pd^0 and Pd^{II} compounds can be summarised. The initial stage of the reaction of molecular hydrogen with Pd^{II} and Pd^0 compounds is the formation of a bound molecular complex in which H_2, acting as an isolated ligand, occupies a vacant position in the coordination sphere of Pd. The electronic factors facilitating the heterolytic rupture of the H–H bond in the reaction of H_2 with Pd^{II} complexes are the high basic strength of the anionic ligands and the involvement of the outer 5*s* and 5*p* AO of the Pd atom. The fact that the oxidative addition of H_2 to one Pd atom in Pd^0 compounds is unfavourable is related to the appreciable expenditure of energy required to give the Pd atom the configuration d^9s^1 necessary for the formation of covalent Pd–H bonds. The greater ability of phosphine complexes of Pt^0 to undergo the dissociative addition of H_2, compared with phosphine complexes of Pd^0, is due to the greater ease of $d \rightarrow s$ and $d \rightarrow p$ promotion in the case of platinum. The dissociative chemisorption of molecular hydrogen on metallic palladium is due to the multicentre interaction of the H atoms of the dissociating molecule with several metal atoms on the surface.

2. The Study of Hydroxopalladation

The practical importance of hydroxopalladation as an effective industrial method for obtaining carbonyl compounds from alkenes[7] is responsible for the interest in the mechanism of nucleophilic addition to the double bond, catalysed by palladium(II) complexes. It has been established experimentally,[7,9,10] that under the conditions of the reaction, the mononuclear π-complexes $PdCl_2(OH)(C_2H_4)^-$ and $PdCl_2(H_2O)(C_2H_4)$, and also the dinuclear derivatives $Pd_2Cl_5(OH)(C_2H_4)^{2-}$ and $Pd_2Cl_5(H_2O)(C_2H_4)^-$, are formed.

It is considered[115] that the hydroxo-complexes can be converted into σ-bonded organopalladium compounds by the inner-sphere *cis*-migration of the coordinated hydroxo-group to the coordinated alkene molecule. In solutions with high concentrations of H_3O^+ ions and (or) Cl^- ions, however, when the formation of hydroxo-complexes is hindered, according to Ref.116 *trans*-attack by the non-coordinated nucleophile on the coordinated alkene molecule takes place, that is the reaction involves an outer-sphere mechanism.

CNDO[36,104] and EHM[103] calculations have been carried out for nucleophilic *trans*-attack in model palladium π-complexes. *cis*-Attack in alkene complexes of Pd^{II} and nucleophilic addition in hydroxomercuration have also been studied.[36]

A mechanism has been proposed[115] for the stabilisation of the intermediate state in *cis*-attack by a coordinated hydroxo-group on a coordinated alkene. According to this mechanism,[115] the approaching ligands form a "quasi-π-allyl" orbital system. The electron density on the C atom closest to the nucleophile decreases, and that on the neighbouring C atom of the double bond increases. The stabilisation of the transition state in this case may be due to the donor–acceptor transfer of electron density from a non-bonding orbital of the quasi-allyl fragment to orbitals of the central atom.[117] In the case of square planar Pd^{II} complexes, this acceptor orbital is the partly filled $4d_{x^2-y^2}$ AO of palladium. As noted in Ref.115, the presence of the partly filled *d* orbital in Pd^{II} may facilitate nucleophilic *cis*-attack for the palladium systems, compared with the corresponding process for Hg^{II} complexes with the electron configuration d^{10}.

The results of a comparative calculation[36] for nucleophilic *cis*-attack on the alkene in the systems $[PdL_2(C_nH_{2n})(OH)]^-$ and $HgX(C_nH_{2n})(OH)$, where X = F, Cl, or Br, and $C_nH_{2n} = C_2H_4$, C_3H_6, or C_4H_8, confirm the proposed[115] "quasi-π-allyl" stabilisation mechanism. In accordance with the "quasi-allyl" model, it was found[36] that the alkene is appreciably polarised by the nucleophilic group. Thus for

$PdCl_2(C_2H_4)(OH)^-$, the effective charge of the C atom closest to OH^- is +0.12e, whereas the charge on the farther removed C atom is −0.32e. The contributions of the 4*d* AO of the Pd atom to the Pd–C and Pd–O bonding interactions are much greater than the corresponding contributions of the 5*d* AO of the Hg atom in the systems $Hg(C_nH_{2n})(OH)$.

A calculation[36] for intermediate structures $PdCl_2(OH)(C_3H_6)^-$ corresponding to nucleophilic attack at different atoms of propene showed that nucleophilic attack at the less extensively hydrogenated position of the alkene is facilitated by the polarisation of the alkene molecule as a result of the hyperconjugation of the methyl group. This explains why Markovnikov's rule is obeyed in this reaction.

To determine the role of the central atom in nucleophilic *trans*-attack on a coordinated alkene, a comparative calculation was carried out[103] for the addition of the hydride ion to ethylene in the model systems $H^-...C_2H_4$ and $H^-...(C_2H_4)PdCl_3^-$. The reactivity of coordinated ethylene towards the addition of H^- depends markedly on the nature of the coordination of ethylene to palladium.

The reaction of H^- with the symmetrical π-complex $(\eta^2\text{-}C_2H_4)PdCl_3^-$ is less favourable than the reaction with free ethylene. The deactivation of coordinated ethylene is due to the increase (compared with free ethylene) in the energy of the lowest unoccupied π*-MO, which makes the main contribution to the interaction of the symmetrically coordinated ethylene with H^-.

The displacement of ethylene with a change from the symmetrical coordination of the η_2-type to coordination of the η_1-type causes H^- attack to be facilitated, compared with free ethylene. This is due to the increase in the strength of the bond formed by Pd with the nearest C atom, and the corresponding localisation of the LUMO on the farther removed C atom, which is attacked by the nucleophile. There is a particularly large change in the contribution of the π-orbital of C_2H_4 to the bonding; in the original structure, the interaction of this orbital with the 1*s* AO of the H atom is a repulsion, whereas in the structure with unsymmetrical coordination of ethylene the π-orbital makes a significant contribution to the $H^-...C_2H_4$ bonding interaction.

Thus it is the possibility of unsymmetrical coordination of the alkene to the central Pd atom in the intermediate state of the nucleophilic *trans*-addition that is responsible for the activation of the alkene in this reaction. The approach of the HO^- ion to the ethylene molecule might have led to the production of the carbanion $CH_2CH_2OH^-$. The formation of this species, however, is energetically so unfavourable that ethylene (unlike acetylene, whose antibonding orbitals are slightly lower than those of ethylene) not only does not react with the hydrated OH^- ion but also does not even react with fused NaOH. The function of the palladium atom in the scheme examined[103] evidently reduces to the stabilisation of the unstable carbanion produced. A comparative calculation for the systems $H^-...(C_2H_4)ML_n$, where ML_n = $PdCl_3^-$, $PtCl_3^-$, $(C_5H_5)_2WH^+$, $Fe(CO)_5^{2+}$, $Fe(CO)_4$, $(C_5H_5)Fe(CO)_2^+$, and $Ni(PH_3)_2$, showed that palladium and platinum have the greatest ability to activate alkenes towards nucleophilic addition.

Calculations[36] for the nucleophilic *trans*-attack by the hydroxide anion in model complexes of Pd^{II} and Hg^{II} indicate that the reactivity of the fragment ML_n towards *trans*-attack by OH^- increases with increase in its acceptor power, which can be estimated from the extent of the transfer of electronic charge from X in the complexes $X[ML_n]^q$. Calculations for the complex $PdX_3(C_2H_4)^-$ and the hypothetical π-complexes $[Hg(C_2H_4)]^{2+}$ and $[HgX(C_2H_4)]^+$, where X = F, Cl, Br, showed[36] that the electron density on the C atom decreases on going from free ethylene to ethylene coordinated to Pd^{II}, and decreases further on going to ethylene coordinated to Hg^{II}. The strength of the C...O bond formed in the nucleophilic addition of OH^- increases in the same order. The quantum-chemical data obtained agree with the difference in the kinetics of the corresponding reactions; hydroxomercuration is very rapid,[118] hydroxopalladation is slow,[119] and OH^- does not add on to free ethylene in the absence of a catalyst.

An increase in the reactivity of complexes $X[ML_n]^q$ with respect to *trans*-attack by the OH^- anion with increase in the acceptor power of the fragment $X[ML_n]^q$ was also observed for π-allyl complexes.[104] Thus the replacement of the anionic ligand Cl^- (a strong electron σ-donor) by the neutral ligands PH_3 and CO (weaker σ-donors, which also have π-acceptor properties) leads to an increase in the energy of the addition of OH^- and to an increase in the two-centre component of the total energy E_{OC} in the order: $PdCl_2(\pi\text{-}C_3H_5)^- \ll PdCl(PH_3)(\pi\text{-}C_3H_5) < PdCl(CO)(\pi\text{-}C_3H_5) < Pd(PH_3)_2(\pi\text{-}C_3H_5)^+$. The quantum-chemical data obtained agree with the experimentally observed[120] increase in the rate of nucleophilic addition to $[PdCl(\pi\text{-}C_3H_5)]_2$ when triphenylphosphine is added to the reaction mixture.

The EHM has been used[105] to study the stage following the nucleophilic addition in the catalytic oxidation of ethylene to acetaldehyde, that is the decomposition of the β-hydroxyethyl σ-complex (β-palladiumethanol) formed in the preceding stage; this decomposition is accompanied by the intramolecular 1,2-transfer of hydrogen. The authors cited,[105] however, in fact carried out the calculation not for β-palladiumethanol but for the system $M(CH_2\text{–}CH_2\text{=}O)$ with a quinquevalent carbon atom, and this lowers the value of the results of this study.

The above quantum-chemical studies of the separate stages of hydroxopalladation lead to some general conclusions. The electronic factor stabilising the transition state of nucleophilic *cis*-addition to alkenes is the donor–acceptor interaction of the non-bonding orbital of the "quasi-π-allyl" system with the slightly filled orbitals of palladium. In the case of nucleophilic *trans*-attack, the activation of the alkene towards the addition of the nucleophilic group is due to the possible unsymmetrical coordination $L_nM...C_nH_{2n}$. The reactivity of the coordinated alkene increases with increase in the acceptor properties of ML_n.

3. Non-Empirical Calculations for the Model System $PdCH_4$ and the Insertion of CO into a Pd–H Bond

The results of non-empirical calculations by the SCF MO LCAO method in a minimum basis set will be examined for two model reactions: the reaction of methane with a palladium atom[99] and the insertion of CO at the Pd–H bond in the systems $[HPdCO]^+$ and H_2PdCO.[100] In Ref.99 the authors continued for the model system $Pd...CH_4$ the study of the activation of saturated compounds by reaction with a palladium atom, begun in Ref.56 with a calculation for the simplest system $Pd(H_2)$ (see above). The problem of the interaction of saturated hydrocarbons with transition metal atoms or ions is of considerable importance for the theoretical analysis of associative and dissociative chemisorption, and also for an understanding of the key reactions in catalysis by metal complexes, namely oxidative addition and reductive elimination.[121]

For the calculation,[99] three symmetrical structures were selected, in which methane is oriented with one, two, or three H atoms directed towards the Pd atom. As in the case of the $Pd...H_2$ interaction examined above, the results

of the calculation for Pd...CH_4 show that the outer 5*s* and 5*p* AO play an important role in the interaction of the Pd atom with saturated compounds. It is the participation of these orbitals in the bonding that enables the Pd atom with its filled *d* level to act as an electron acceptor in the reaction with methane. The absolute magnitude of the calculated values of the Pd...CH_4 bond energy decreases with increase in the number of H atoms directed towards the Pd atom, but the values are nevertheless close to one another. The equilibrium Pd–H distance also increases in this order.

The energy of the bond formed by molecular hydrogen with the Pd atom, calculated in the same basis set, is almost double the energy of the bond formed by methane.[56] At first sight this result appears strange, since judging from the energy of the LUMO and the experimental ionisation potentials, methane should be a better electron donor than hydrogen. In this case, however, the reaction is determined by the geometric factor, that is not by the difference in the energies of the levels but by the degree of overlap of the filled orbitals of CH_4 with the filled 4*d* and vacant 5*s* and 5*p* AO of the Pd atom.

In the structure in which only one H atom of methane can be in direct contact with the Pd atom, the overlap conditions are responsible for the weaker donor–acceptor interaction compared with H_2. In the structures in which the CH_4 molecule is oriented with two or with three H atoms directed towards the Pd atom, however, the principal role in the interaction with Pd is played by the C atom. The latter has a much larger covalent radius than the hydrogen atom, so that there is a greater Fermi repulsion interaction between the valence electron levels of Pd and CH_4. As a result, the complex of palladium with molecular hydrogen is more stable than the complex with methane.

The results[99] show that methane (and apparently alkanes in general), like hydrogen, can take part in a bonding interaction with the Pd atom in which the most important role is played by the overlap of the localised orbitals of the ligand with the diffuse outer orbitals of the transition metal.

The insertion of CO at a Pd_{surf}–H bond

$$Pd_{surf}-H + CO \rightleftarrows Pd_{surf}-CHO$$

which has been studied[100] by a non-empirical calculation for simple molecular models, is one of the stages (possibly the limiting stage) in the heterogeneous catalytic reduction of CO by hydrogen. The catalyst in this reaction is palladium deposited on an oxide support.[2] In an earlier paper[57] on the calculation of the electronic structure of the model system Pd(CO) the authors cited[100] suggested that the ability to insert CO into the M–H bond to give a formyl complex should increase with increase in the acceptor power of the transition metal. This suggestion is confirmed by experimental data which show that the active species in the reduction of CO are ionic forms of Pd stabilised by the carrier. It has also been found that the rate of the reduction of CO by hydrogen on palladium catalysts increases with increase in the electron–acceptor properties of the carrier.[2]

The dependence of the direction and the energy barrier of the migration on the magnitude of the effective charge on the Pd atom has been studied[100] by comparative calculations for the model systems $[HPdCO]^+$ and H_2PdCO. The first models the limiting case of a strongly electron-accepting environment; the second, which differs from the first in the addition of the hydride ion, which is a strong σ-donor, models the coordinative saturation of Pd in an electron-donor environment. For each system, the calculations were carried out for three structures: the original carbonyl hydride structure, an intermediate structure with a bridging Pd–H–C bond, and the final formyl structure. It was found that the addition of the hydride ion leads to a complete qualitative change in the nature of the potential curve for the migration of H to the CO group. The $[HPdCO]^+$ system can be regarded as structurally non-rigid, since there is no energy barrier to migration, and the formyl structure is even slightly more stable than the carbonyl hydride structure. On the other hand, in the case of the H_2PdCO system, the formyl structure is energetically unfavourable, and the barrier for the reverse reaction of elimination is ~15 kcal mole^{-1}. The fact that the migration of H to CO is energetically unfavourable in the last case is due to the extensive population of the 5*s* and 5*p* AO of palladium, preserved throughout the reaction.

From these results it was concluded[100] that, in agreement with experimental data, the increase in the positive charge on the Pd atom accompanying an increase in its acceptor power favours the relative stabilisation of the formyl structure. Correspondingly, an increase in the acceptor properties of the carrier may facilitate the formyl mechanism of the reduction of CO by hydrogen on palladium catalysts.

Thus the energy effect of the above model reactions and the electron density distribution accompanying them depend to a significant extent on the participation of the outer 5*s* and 5*p* AO of the Pd atom in the bonding interaction.

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The above review of the results of quantum-chemical studies shows that the electronic structure and reactivity of palladium compounds are determined to a large extent by the characteristic features of the electronic structure of the Pd atom. These characteristic features, as noted above, are the complete filling of the 4*d* level in the ground state of the atom and the presence of diffuse outer 5*s* and 5*p* AO.

Further progress in the understanding of the mechanism of the reactions of palladium compounds will probably be associated to a large extent with the accumulation and analysis of experimental and theoretical data on the electronic character and relative strength of Pd–L bonds in series of complexes of different transition metals. In particular, the study of the electron density distribution in palladium systems in order to determine the preferred direction of attack on these complexes by different reagents is of considerable interest.

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The Interconversions of Pyrylium Salts, Pyrans, Pyrones, and Their Open-chain Forms

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A general scheme is proposed for the interconversions of six-membered oxygen-containing heterocylces (pyrylium salts, pyrans, and pyrones) and their open-chain forms, having selected pyrylium salts as compounds of the key type. The latest data concerning the mechanism of a number of the above transformations are examined. It is shown that ring opening is one of the most characteristic manifestations of the reactivity of six-membered oxygen-containing heterocylces.
The bibliography includes 231 references.

CONTENTS

I. Introduction 1167
II. Pyrylium salts-2*H*-pyrans-*cis*-dienones 1168
III. Pyrylium salts-4*H*-pyrans 1171
IV. 4*H*-Pyrans-2*H*-pyrans-*cis*-dienones 1172
V. Pyrylium salts-pseudobases of pyrylium salts 1173
VI. 4*H*-Pyrans-saturated 1,5-diketones 1175
VII. Saturated 1,5-diketones-pyrylium salts 1175
VIII. α-Pyrones-saturated 1,5-diketones 1177
IX. α-Pyrones-2*H*-pyrans 1177
X. γ-Pyrones-γ-pyranols-pyrylium salts 1180

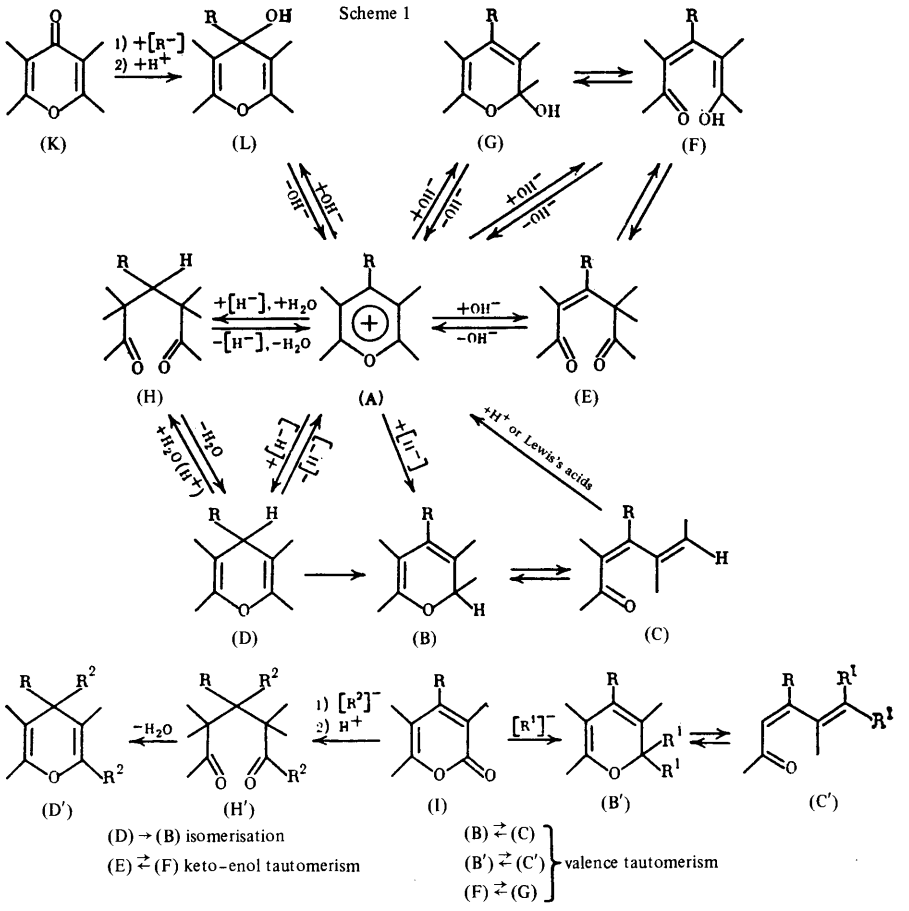
I. INTRODUCTION

Six-membered oxygen-containing aromatic and non-aromatic heterocycles (pyrylium salts, 2*H*- and 4*H*-pyrans, α- and γ-pyrones, and α- and γ-pyranols) and their open-chain forms (pentene-1,5-diones, pentadien-5-ones, pentane-1,5-diones, etc.) are readily interconverted. Individual aspects of these reactions have been the subject of studies since the beginning of this century, but investigation of the problem in terms of the complete set of its general and specific properties has become possible only recently. This has been promoted, particularly, by the application of physicochemical methods (spectroscopic and electrochemical) in practical chemical studies, by the investigation of kinetics, and also by the expansion of synthetic possibilities, for example, as a result of the vigorous application of organometallic compounds.

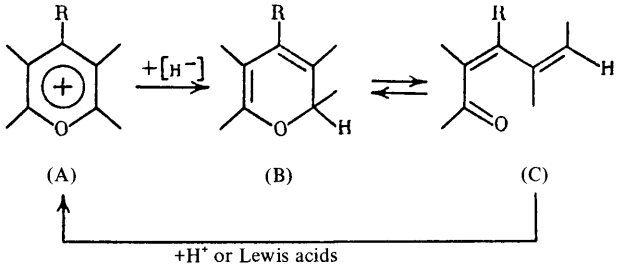
In the present review we propose a general scheme for the above reactions involving a fundamental class of heterocycles, namely pyrylium salts[1-14] (Scheme 1), as compounds of the key type. In the course of the exposition we shall deal with individual fragments of this scheme which reflect the most characteristic transitions undergone by the classes of compounds included in it†.

† In view of the complexity of the structures of the 1,5-diketones (H′) and 2*H*-pyrans (B′) formed, which are incapable of participating in the majority of the reactions considered, the transitions (I)–(H′) and (I)–(B′) are included in addition to the main scheme. We may point out, however, that diketones of type (H′) are capable of being dehydrated to 4,4′-disubstituted 4*H*-pyrans (D′) and 2*H*-pyrans (B′), which can undergo valence isomerisation to the *cis*-dienones (C′). In order to simplify Scheme 1 the addition and elimination of a hydride ion are considered in the case of the (A)–(D) transition, while the reactions of pyrilium salts with other compounds, leading to 4*H*-pyrans with a more complex structure, are dealt with in the text. Similarly the scheme indicates only the effect of the hydride ion for the (A)–(D) transitions. Other instances of the synthesis of 2*H*-pyrans on the basis of pyrylium salts are described in the text. The OH^- anion has been adopted as the effective species in the (A)–(L), (A)–(E), (A)–(F), and (A)–(G) transitions; more complex examples involving alkoxy-groups are discussed in the text.

Scheme 1



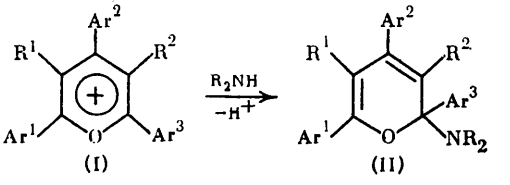
II. PYRYLIUM SALTS–2*H*-PYRANS–*cis*-DIENONES



Alkali metal tetrahydroborates ($NaBH_4$, $LiBH_4$, and KBH_4) react with pyrylium salts to form unstable 2-monosubstituted 2*H*-pyrans (B),[15–20] which rapidly isomerise to the corresponding *cis*-dienones (C). It is striking that in all cases the interaction of complex metal hydrides with pyrylium salts leads to the formation, together with the above compounds, also of 4*H*-pyrans (D) and their open-chain forms—saturated 1,5-diketones.[3]

Comparatively stable 2*H*-pyrans of type (B) and their valence tautomers, i.e. *cis*-dienones (C), are synthesised also by the reaction of pyrylium salts (A) with organometallic reagents (not included in the Scheme).[21–31]# Since the positive charge on the pyrylium cation is concentrated in the 2-, 4-, and 6-positions, as has been confirmed by quantum-chemical calculations,[12,14] 4*H*-pyrans are formed together with 2*H*-pyrans. The ratios of the products formed (2*H*-pyrans, *cis*-dienones, and 4*H*-pyrans) are determined by the structure of the pyrylium salt, the nature of the nucleophile, and the reaction conditions.

When pyrylium salts (I) are treated with dialkylamines in aprotic solvents (for example in diethyl ether), stable 2*H*-pyran derivatives (II) can be isolated in a crystalline form:[36]

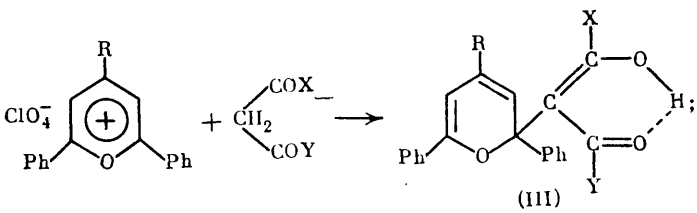


R^1 = H, Me; R^2 = Me .

#2*H*-Pyrans[32] can also be obtained by treating α-pyrones with organometallic reagents (Section IX), in the course of the isomerisation of 4*H*-pyrans (Section IV), and as a result of cyclocondensation[33–35] with participation of carbonyl compounds.

The authors[36] explained the stability of the 2*H*-pyrans (II) by the presence of substituents in the 3- or 3- and 5-positions in the pyrylium ring.

Pyrylium salts are also capable of reacting with CH acid compounds to form 2*H*-pyran derivatives. They are formed, for example, in the reaction of 2,4,6-triphenylpyrylium tetrafluoroborate with acetonedicarboxylic acid or acetylacetone.[4] The method of phase-transfer catalysis provides much greater possibilities for the synthesis of 2*H*-pyrans involving CH acid compounds.[37] 2*H*-Pyrans (III, a–g) have been obtained by this method in the reaction of 2,4,6-triphenyl and 2,6-diphenyl-4-(α-thienyl)-pyrylium perchlorates with acetoacetic ester, acetylacetone, and malonic ester:



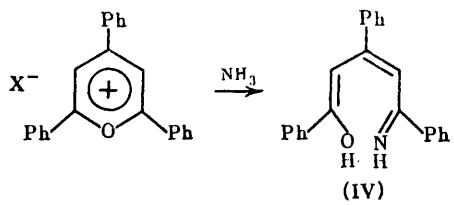
(III)

(a) R=Ph, X = Me, Y=OEt, (b) R=Ph, X=Y=Me, (c) R=Ph, X=Y=OEt; (d) *R*= , X=Y=OEt .

The isolation of the 2*H*-pyrans (III, a–g) confirms the mechanism proposed previously[5] for the reaction of pyrylium salts with active methylene groups in which the intermediate formation of 2*H*-pyrans was postulated. One of them, namely compound (Ib), has been isolated[15] in the reaction of 2,4,6-triphenylpyrylium tetrafluoroborate with acetylacetone in the presence of 1 mole of potassium t-butoxide, but its structure has not been rigorously confirmed.

The appearance of 2*H*-pyrans of type (B) is usually postulated as the first stage in the interaction of pyrylium salts (A) with various nucleophiles, leading either to recyclisation products[11–14] or to ring opening products.[8,14]§ The latter are frequently intermediates in the recyclisation of pyrylium salts; if these products are stable, the reaction terminates with their formation. The reactions of 2,4,6-trisubstituted pyrylium salts with N-containing and certain other nucleophiles, in which ring-opening products with different stabilities can be obtained, are examples of the second of the competing processes indicated.

Thus the reaction of a pyrylium salt with ammonia can lead to the isolation of the ring opening product—the relatively unstable iminoenol (IV):[38]

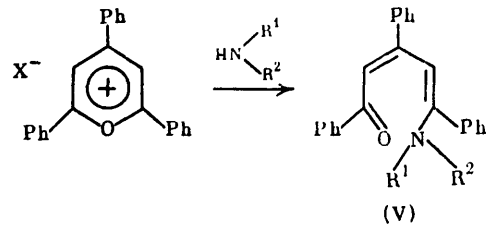


(IV)

When pyrylium salts are acted upon by amines, there is a possibility of the formation of aminopentadienones (V).[39,40]

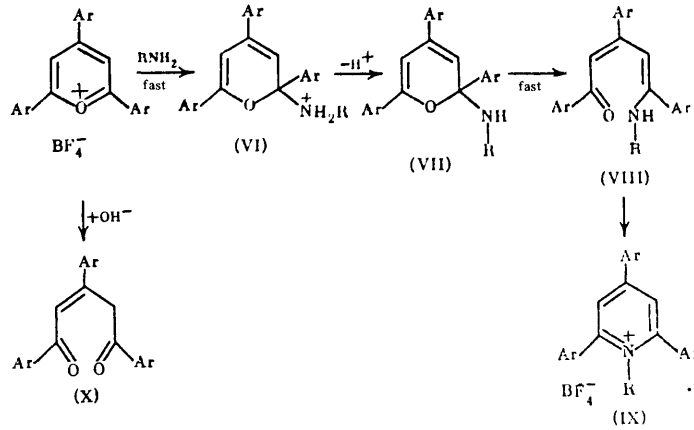
§ These products can be regarded as derivatives of the diketone forms of the pseudobases of pyrylium salts formed via the keto-groups.

In the case of primary amines the yields of compound (V) are low, while in the reaction involving secondary amines they are satisfactory:



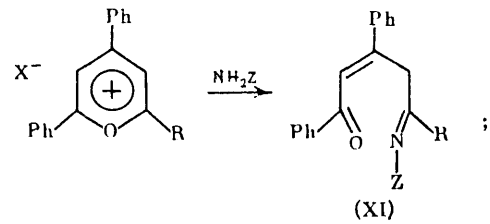
(V)

The interaction of pyrylium salts with amines has been studied in detail by Katritzky and co-workers.[41,42] The reaction pathway and the structure of the substances formed were studied, in particular, by ^{13}C NMR:



When two moles of a primary amine are introduced into the reaction, pyridinium salts (IX) are formed in quantitative yields, but, when less than two moles of the amine is used, the amount of the side product, the unsaturated diketone (X), increases. Under the reaction conditions, the latter also gives rise to a pyridinium salt, but this reaction is very slow. The authors[42] assume that the second amine molecule is necessary to abstract a proton from the intermediate (VI). The pyrylium salt which failed to react is converted by traces of water into the pentenedione (X). In particular, the reactions with n-butylamine and benzylamine take place in this way. Pyrrolidine and piperidine have been used as secondary amines. The reaction of pyrylium salts with 2 moles of a secondary amine leads to the formation of aminopentadienones of type (VIII), which do not cyclise to pyridinium salts.

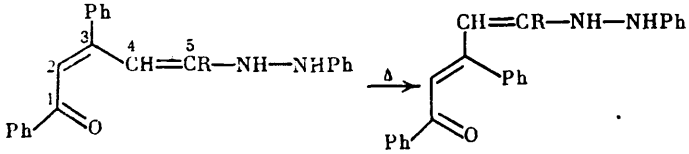
The fairly stable monoxime (XIa) and the monophenylhydrazone (XIb) are formed when a pyrylium salt interacts with hydroxylamine[43] and phenylhydrazine:[43,44]



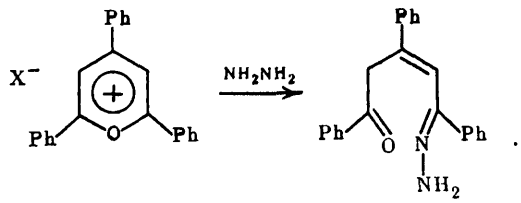
(XI)

(a) R=Ph, Z=OH; (b) R=Ph, Me; Z=NHPh .

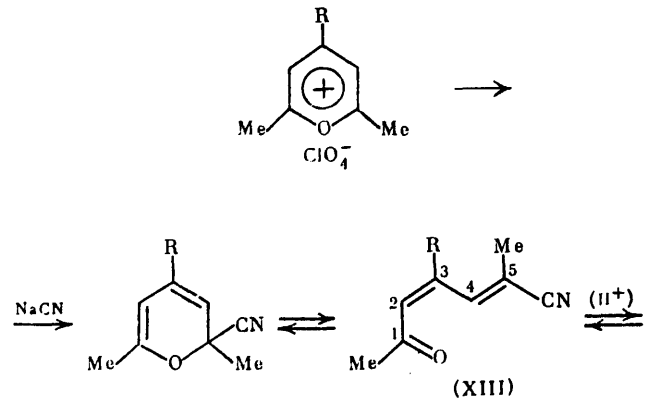
The monophenylhydrazone (XIb) is also formed as the *cis*-isomer [with a *cis*-disposition the carbonyl group and the CH=CR–NH–NHPh group relative to the C(2)=C(3) double bond], which is converted into the *trans*-isomer on refluxing in a neutral medium (ethanol):



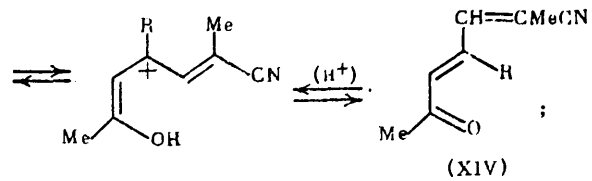
When the 2,4,6-triphenylpyrylium salt is acted upon by hydrazine hydrate, the unstable monohydrazone (XII) is formed:[45,46]



(XII)



(XIII)

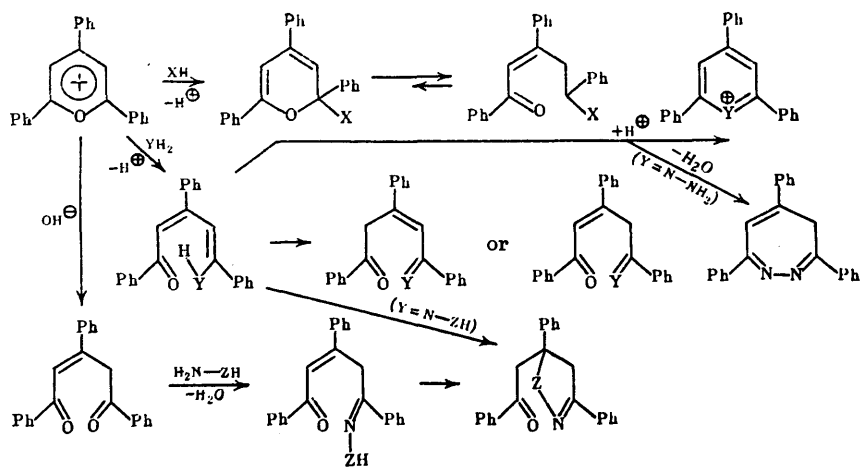


(XIV)

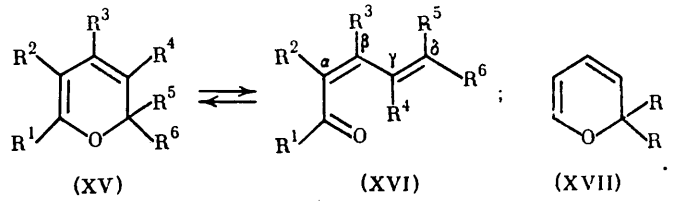
R = Me, Et.

The ring opening products in the reaction of 2,4,6-trialkylpyrylium salts with cyanides are the *cis*-cyanopentadienones (XIII). On treatment with concentrated inorganic acids, the latter react via two pathways: they are reconverted into the initial pyrylium salt, liberating hydrogen cyanide, and they isomerise to the *trans*-pentadienones (XIV). The *cis,trans*-isomeric forms are determined by the relative positions of the carbonyl group and the CHCMeCN group relative to the C(2)=C(3) double bond:[47,48]

The products of the opening of the ring in pyrylium salts, which can also be regarded as the open-chain forms of 2*H*-pyrans, are capable, as already stated above, or different types of subsequent cyclisation with formation of various heterocyclic systems. For example, compounds (IV), (V), (XIa), (XIb), and (XII) cyclise with formation of the corresponding nitrogen-containing heterocycles—pyridine, pyridinium salts, isoxazole, pyrazoles, and diazepine, as shown in the general scheme published by Balaban and Silan:[49]



The phenomenon of valence isomerism, a symmetry-allowed thermal pericyclic process[52] with a low activation energy, is characteristic of the class of 2*H*-pyrans.[50,51] It results in the establishment of a rapid and reversible equilibrium between the 2*H*-pyrans (XV) and their valence tautomers—the *cis*-dienones (XVI)¶:[53–79]



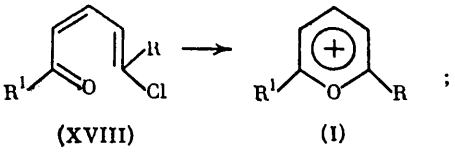
(XV) (XVI) (XVII)

For this very reason, the parent compound of the class of 2*H*-pyrans, namely unsubstituted pyran, has not so far been obtained. Quantum-chemical calculations of the stability of the valence isomers (XV) and (XVI)[80–83] give preference to the cyclic form (XV). In the course of the analysis of the pathways leading to the valence photo- and thermo-isomerisation of the 2*H*-pyran ring, taking into account the characteristic features of the electronic structure of the transition state in the reaction

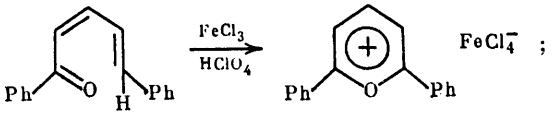
$$(XV) \underset{}{\overset{h\nu, kT}{\rightleftharpoons}} (XVI),$$

a correspondence has been observed between the energy barrier to the opening of the pyran ring and the C_{sp^3}–O bond length.[83] At the same time *ab initio* calculations have shown that open-chain forms with different geometries are more stable for both the 2*H*-pyran (XVII, R = H)[80] and its diemthyl derivative (XVII, R = Me).[82]

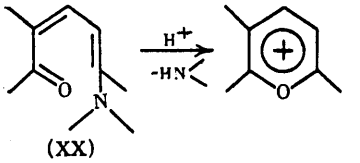
The reverse transformation of 2*H*-pyrans into pyrylium salts (A), which is characteristic of 4*H*-pyrans (D), has not been observed in the case of the 2*H*-pyran (B). However, compounds which are derivatives of dienones, for example, (XVIII)–(XXI), readily cyclise with formation of pyrylium cations:[60,84–87]



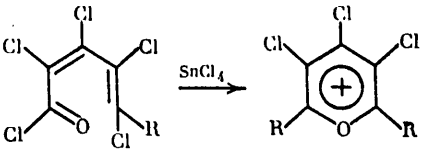
(XVIII) (I)



(XIX)

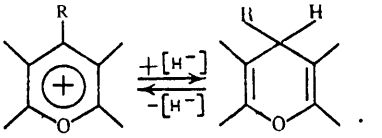


(XX)



(XXI) $SnCl_5^-$

III. PYRYLIUM SALTS–4*H*-PYRANS



(A) (D)

The transformation of pyrylium salts (A), usually with a free γ-position (R = H), into 4*H*-pyrans (D) constitutes the most thoroughly developed method of synthesis of the latter and is achieved by reduction with complex metal hydrides.[26–31,88–91] However, the methods of synthesis of 4*H*-pyrans from pyrylium salts are not restricted to this simplest case. 4-Substituted or 4,4'-disubstituted 4*H*-pyrans are also formed as a result of reaction with CH acid compounds in the presence of catalysts,[15,92–94] by reaction with organic and inorganic nucleophiles in the absence of catalysts,[95–105] with the aid of organometallic synthesis,[106–122] and by many other procedures.[123–127] The reaction of 2,4,6-trisubstituted pyrylium salts with strong nucleophiles (Grignard reagents, organolithium compounds, or complex metal hydrides) results in the formation, together with 4*H*-pyrans (D), of 2*H*-pyrans (B) and their valence isomers—*cis*-dienones (C). In an acid medium the open-chain form of the 4*H*-pyran, namely a saturated 1,5-diketone, is isolated instead of the 4*H*-pyran itself.

The reduction and dimerisation of pyrylium salts under the influence of electron donors lead to the formation of bis-4*H*-pyrans.[111,128–130]†

4*H*-Pyrans[120] are compounds of a comparatively unstable type. The unsubstituted 4*H*-pyran, which was obtained as late as 1962 from glutaric dialdehyde,[144] is a colourless liquid, which rapidly decomposes in the light at room temperature.[144,145] The introduction of substituents stabilises the pyran ring, but in this case they are frequently isolated in

¶ The dienones can exist as the *cis*- or *trans*-isomers with respect to the αβ-double bond.[44,48,75] It has been shown that only one geometrical isomer is involved in the dienone–2*H*-pyran equilibrium.[18,75] From this and also from the hypothesis that the valence isomerisation can involve only the geometrical isomer with the minimum distance between the C=O group and the C_δ atom, it has been concluded[75] that this isomer exists in the *cis*-form. Direct observation by means of ^{1}H NMR has confirmed this claim, which had been accepted previously without adequate evidence.[66,68,70,71]

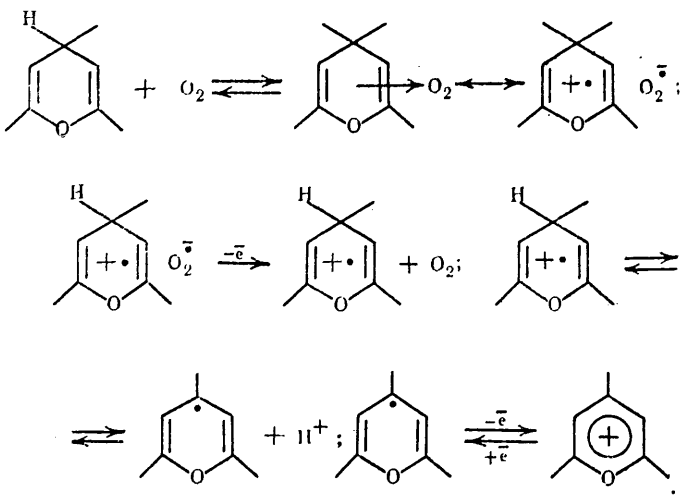
† Apart from the synthesis from pyrylium salts, 4*H*-pyrans can be obtained also by condensation involving carbonyl compounds[131–143] and by the cyclisation of 1,5-dicarbonyl compounds.[117,131,145]

the form of non-crystalline oils which are difficult to purify.[4, 16,89,107,110,111,131] On storage, many crystalline pyrans "deliquesce", but 4*H*-pyrans with carbaboranyl substituents are more stable.[113–121]

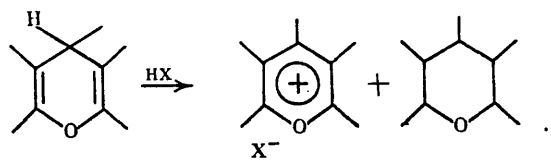
4*H*-Pyrans (D), containing a hydrogen atom in the γ-position and therefore capable of undergoing oxidative dehydrogenation, serve as convenient starting materials in the synthesis of pyrylium salts (A). 4*H*-Pyrans are dehydroaromatised with the aid of acetyl perchlorate,[108–111,115,117,119,120] triphenylmethyl perchlorate,[99,102,103,121,122,125] PCl_5,[117,125] $FeCl_3$,[4] CCl_3,[110,111,120] 2,4,6-tri-t-butylcyclohexadienone,[110,111] the tris(*p*-bromophenyl)aminium radical-cation,[110–114,116,117,120] benzenediazonium tetrafluoroborate,[110,111] tropylium tetrafluoroborate,[88] bis(2,4-dimethoxyphenyl)immonium perchlorate,[115,116,120] etc.

The transfer of a hydride ion is observed in almost all classes of organic compounds and has been the subject of controversy.[146,147]

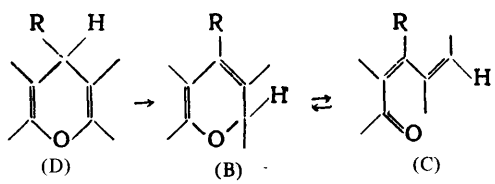
Okhlobystin and co-workers[148] investigated the dehydroaromatisation of pyrans by EPR and electrochemically; they also proposed a stepwise mechanism for this process, which is vigorously catalysed by oxygen. They suggest that the substrate undergoes one-electron oxidation in the decisive stages:



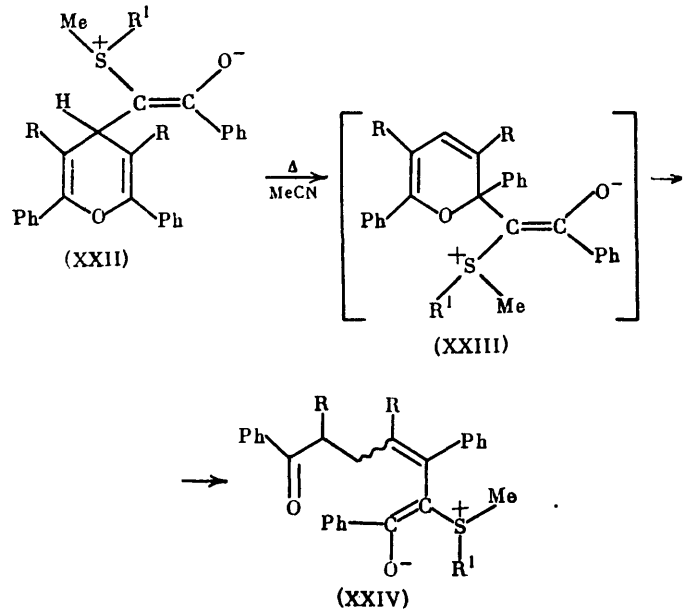
The ability to disproportionate under the influence of acids (protic and aprotic), which results in the formation of a pyrylium salt and a tetrahydropyran, is also characteristic of 4*H*-pyrans:[149,150]



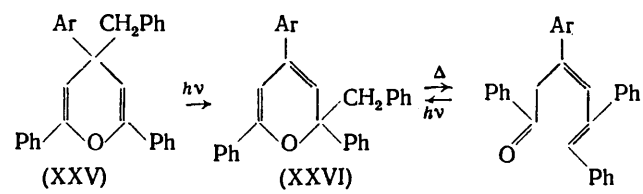
IV. 4*H*-PYRANS–2*H*-PYRANS–*cis*-DIENONES



4*H*-Pyrans (XXII)#, containing an ylide group in the 4-position, give rise to the open-chain compounds (XXIV) in the form of two geometrical isomers in the course of their thermal rearrangement.[151] There is no doubt that the first stage in the rearrangement involves the formation of 2*H*-pyrans (XXIII), which then undergo valence isomerisation to the corresponding dienones (XXIV):



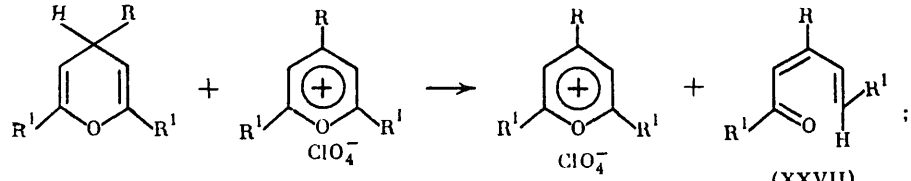
When the 4*H*-pyrans (XXV), containing the benzyl group in the γ-position, are irradiated, they readily give rise to the corresponding 2*H*-pyrans (XXVI):[152–155]



The 2*H*-pyrans (XXVI) undergo thermal isomations to non-conjugated dienones, which recyclise to the 2*H*-pyrans on irradiation. The migration of the benzyl group on photoisomerisation of 4*H*-pyrans proceeds via a singlet mechanism. The positions of the double bonds and of the substituting groups in the isomeric heterocycle are indicated by its ability to react with maleic anhydride, to form a transannular peroxide on sensitised photochemical oxidation, etc.

The hydride mobility of 4*H*-pyrans in relation to 2*H*-pyran and its open-chain isomer (a dienone) has been investigated;[90] pyrylium cations were used as hydride ion acceptors. Treatment of 2,6-triphenyl-4*H*-pyrans with the corresponding pyrylium cation leads to the formation of cinnamylideneacetophenone (XXVIIa) and 1,3,5-triphenylpenta-2,4-dienone (XXVIIb):

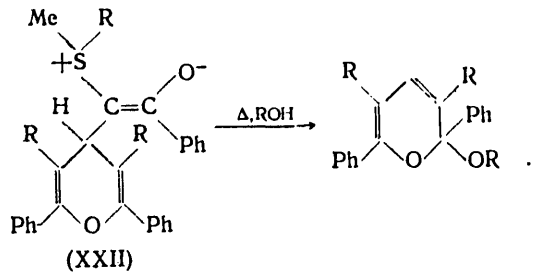
#The isomerisation of the 4*H*-pyrans (D) to 2*H*-pyrans (B) is given a conventional representation in Scheme 1, since it has been simplified by indicating hydrogen as the migrating species.



(a) R^1 = Ph, R = H; (b) R = R^1 = Ph.

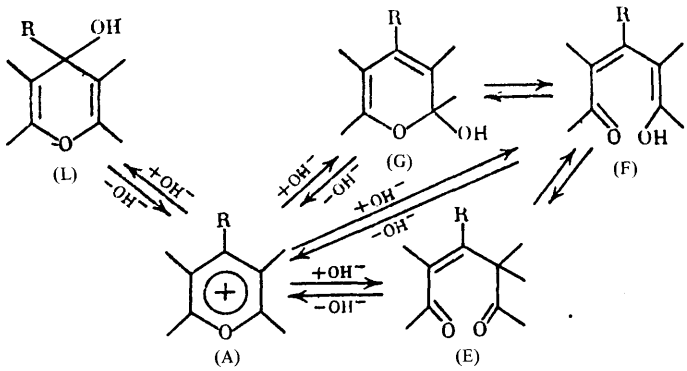
Thus it has been shown that the 2*H*-pyran is formed in the hydride transfer from the 4*H*-pyran to the 2-position in the pyrylium ring. On valence isomerisation, the 4*H*-pyran gives rise to the more stable open-chain form. In other words, 4*H*-pyrans (D) are less stable than 2*H*-pyrans (B), which are in their turn less stable than their isomeric *cis*-dienones (C).

The thermal rearrangement of the 4*H*-pyrans (XXII), containing the sulphonium ylide group in the γ-position, in methanol or ethanol results in the formation of the corresponding alkoxy-2*H*-pyrans:[151]



(XXII)

V. PYRYLIUM SALTS–PSEUDOBASES OF PYRYLIUM SALTS

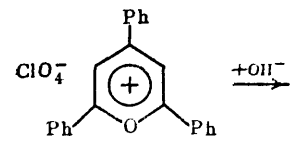


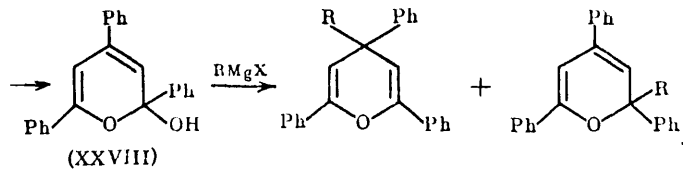
The products of the addition of *O*-nucleophiles (hydroxide and alkoxide anions) to the α- and γ-positions in pyrylium salts are referred to as the pseudobases (E)–(G) and (L).[156] Stable pseudobases have been obtained from arylpyrylium salts. Alkylpyrylium salts give rise to sensitive and unstable pseudobases, which cannot be isolated. The crystalline 4-methyl-2,6-di-t-butylpyrylium pseudobase, which can be stored for several minutes at room temperature, is an exception.[12]

The structure of the substances formed on reaction of pyrylium salts with *O*-nucleophiles is determined mainly by the structure of the initial pyrylium cations and also by the character of the reagent and has been established unambiguously only recently when spectroscopic methods (infrared, ultraviolet, and NMR spectroscopy) and X-ray diffraction methods have become available.

The first stage in the reaction of pyrylium salts with the hydroxide anion, like that in the reactions with other nucleophiles, may involve the attack on the α- or γ-position with formation of the 4-pyranol (L) or the 2-pyranol (G), which is then converted into the pentene-1,5-dione (E) (in the *cis*- or *trans*-form) or the enolic tautomer (F)§.

The hydrolysis of 2,4,6-triphenylpyrylium perchlorate in a highly alkaline medium (pH 14) yielded the corresponding α-pyranol (XXVIII)[157] in conformity with the fact that the α-positions are more reactive:[12]





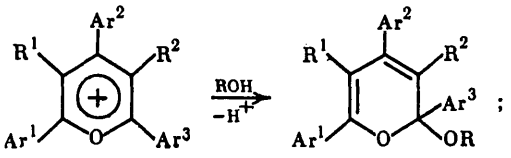
(XXVIII)

The concentration of hydroxide ions was kept constant by means of a buffered methanolic solution. On reaction with organometallic reagents, the α-pyranol produces substituted 2*H*- and 4*H*-pyrans.

The formation of 2-methoxy-2*H*-pyrans on interaction of pyrylium salts with the methoxide anion has been demonstrated by kinetic methods[158,159] and also by ^{1}H NMR [160] and ^{13}C NMR.[42] 4-Methoxy-4*H*-pyran is formed together with 2-methoxy-2*H*-pyran.[158,159] There is also a possibility of the formation of the corresponding *cis*-dienone instead of 2-methoxy-2*H*-pyran.[158,159] The ratio of the above products is determined by the structure of the initial pyrylium salt and the reaction conditions. For example, it has been shown that 2,4,6-triarylpyrylium salts having substituents in the 3- or 3- and 5-positions in the pyrylium ring give rise to stable crystalline 2-alkoxy-2*H*-pyrans on treatment with alkali metal alkoxides:[161]

---

§Because of the conventional nature of the general scheme (1), the OH^- anion has been adopted as the O-nucleophile in the fragments having a bearing on the formation of the pseudobases in order to demonstrate in a more clear-cut form the possibilities for the interconversions of compounds (A), (E), (F), (G), and (L).

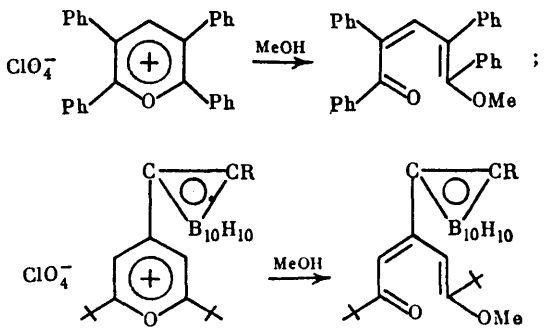


R^1 = H, Me; R^2 = Me, $PhCH_2$.

However, as a rule open-chain forms (pentene-1,5-diones or ketodienols) are formed in the course of hydrolysis or alcoholysis. The hydrolysis of, for example, 2,3,5,6-tetraphenylpyrylium[162] and 2,6-di(methoxycarbonyl)pyrylium[163] cations is carried out in an aqueous medium. However, the formation of open-chain forms of the pseudobases is usually observed in hydrolysis in the presence of inorganic and organic bases.

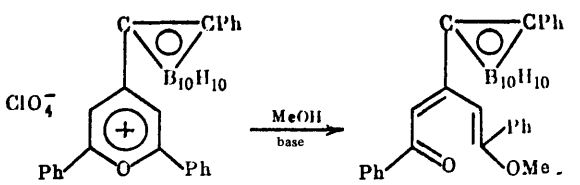
Although the formation of ketodienols is relatively uncharacteristic of pyrylium salts, nevertheless, when the latter are acted upon by alkoxides in the corresponding alcohols, the ketodienol ethers are formed readily. For example, the 2,4,6-triphenylpyrylium cation gives rise to oily methoxy- and ethoxy-derivatives as well as the crystalline isopropoxy-derivative.[49]

2,3,5,6-Tetraphenylpyrylium[162] and 2,6-di-t-butyl-4-carbaboranylpyrylium[164–166] perchlorates readily produce the corresponding stable methyl ethers of ketodienols in the course of methanolysis:



R = Me, Ph.

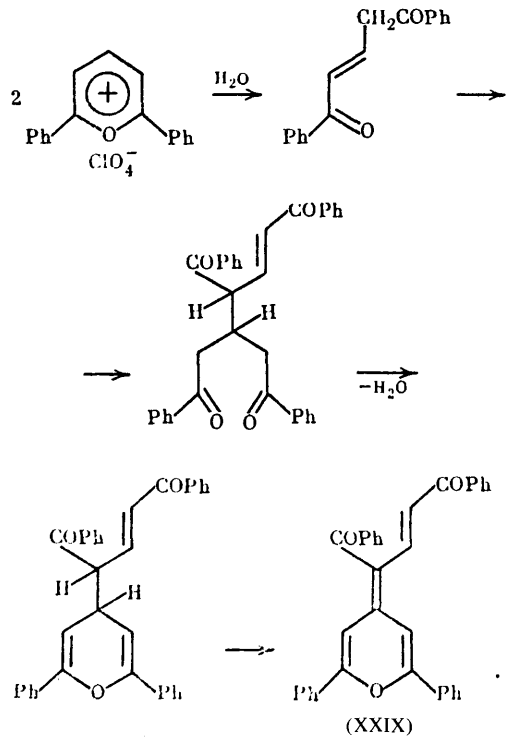
The methanolysis of 2,6-diphenyl-4-(phenyl-*o*-carbaboranyl)pyrylium perchlorate, which leads to the methyl ether of the ketodienol, takes place only in the presence of bases:



The bases used are $NaHCO_3$, MeONa, Et_3N, 5-aminotetrazole, $H_2NC_6H_4COOEt$, NH_2CONH_2, $(PhNH)_2C{=}NH$, $Me_2C{=}NOH$, and Br=NPh [?(Ed.of Translation)].

The formation of the methoxide anion, which has fairly pronounced nucleophilic properties,[167] is apparently induced by various types of acid–base interaction (autoprotolysis of the alcohol, protonation of the amine, etc.). The attack on the pyrylium ring is then undoubtedly facilitated by the electron-accepting effect of the carbaboranyl substituent; cations containing t-butyl groups in the 2- and 6-positions are especially activated.

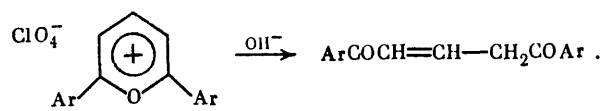
The hydrolysis and alcoholysis of 2,6-diarylpyrylium salts with a free γ-position occupies a special place. On interaction with water in the presence of bases, 2,6-diphenylpyrylium perchlorate affords 1,5-diphenyl-4-(2,6-diphenyl-4-pyranylidene)pent-2-ene-1,5-dione.[168,169] The mechanism of the formation of this compound involves the hydrolysis of the pyrylium salt to an unsaturated diketone, which undergoes Michael self-condensation; the subsequent cyclisation to the 4*H*-pyran and dehydrogenation lead to the pyranylidenediketone (XXIX):



(XXIX)

A similar reaction is common to 2,6-diarylpyrylium salts. The optimum conditions for the syntheis of pentenediones of type (XXIX) involve brief refluxing of an equimolar mixture of 2,6-diarylpyrylium perchlorate with water and pyridine in acetonitrile.

Unsaturated 1,5-diketones having the *trans*-configuration were obtained only on treating 2,6-diarylpyrylium perchlorates with an aqueous acetone solution of alkali:



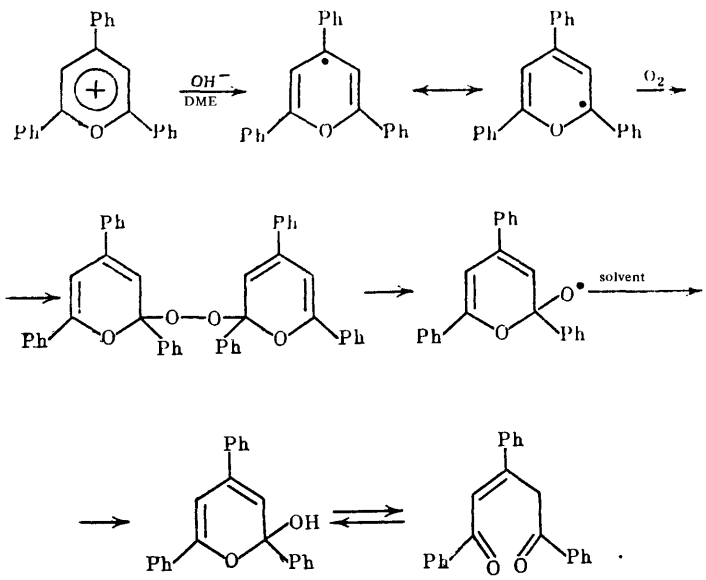
On treatment of 2,6-diarylpyrylium salts with aqueous alcoholic solutions of bases, unstable α-alkoxypyrans are formed; 3-benzoyl-6-ethoxy-6-(*p*-nitrophenyl)-2-phenylpyran was isolated in an analytically pure state. The use of sodium acetate as the base entailed the formation of a complex mixture of acetoxypyrans, whose treatment with acids produced high yields of pyrylium salts with various anions.

The elucidation of the mechanism of the hydrolysis of pyrylium salts leading to the opening of the pyrylium ring is of significant interest. Kinetic methods have been used in a number of studies.[170–172]

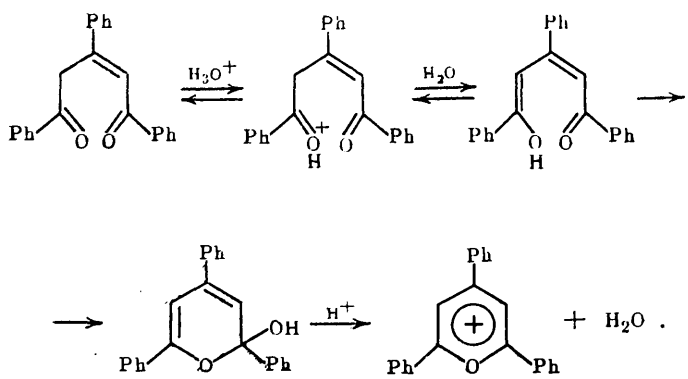
It has been found[173,174] that, on treatment with NaOH in acetone or dimethoxyethane (DME) in the absence of oxygen, 2,4,6-triphenylpyrylium perchlorate is quantitatively converted into the 2,4,6-triphenylpyranyl free radical, which was identified by EPR.

On contact of the reaction mixture with atmospheric oxygen, 1,3,5-triphenylpent-2-ene-1,5-dione is formed. The same diketone has been obtained on oxidising with atmospheric oxygen the free radical arising in the dissociation of the triphenylpyranyl radical dimer.[111]

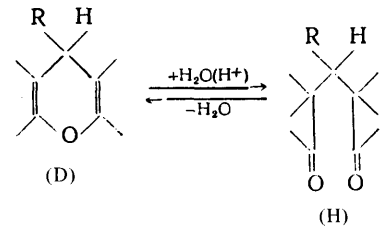
From their data, the authors[173,174] put forward the following mechanism of the formation of unsaturated 1,5-diketones from pyrylium salts:



On treatment with acids, unsaturated 1,5-diketones readily cyclise to pyrylium salts.[41] Kinetic studies of the mechanism of the reactions of the above diketones with H_3O^+ showed that the dione cyclises as a result of the rapid enolisation and subsequent ring closure of the enol to form an unstable 2-hydroxy-2*H*-pyran, which is converted into a pyrylium salt in the presence of protic acid:[175]

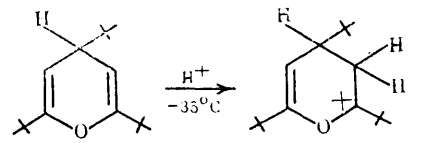


VI. 4*H*-PYRANS–SATURATED 1,5-DIKETONES



4*H*-Pyrans (D)¶ readily undergo ring opening in the course of hydration in an acid medium with formation of saturated 1,5-diketones (H).[16,93,117–120,132,133,163,176–179] Aqueous, alcoholic, or aqueous alcoholic solutions of HCl are then used as a rule and the employment of the strong perchloric acid is essential only for carbaboranyl-4*H*-pyrans.[117–120]

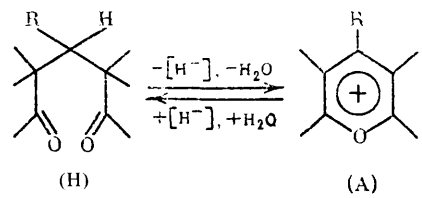
The reaction involving the opening of the pyran ring begins most probably with the protonation of the β-position of the 4*H*-pyran with subsequent addition of the hydroxide anion to the tertiary carbonium ion centre arising in the α-position. For example, it has been shown that the protonated form of 2,4,6-tri-t-butyl-4*H*-pyran, arising in a $FSO_2OH–CS_2$ mixture at −35 °C, gives rise to a well resolved ^1H NMR spectrum, indicating the non-equivalence of the methylene protons in the 3-position:[111]



The reverse reaction involving the cyclisation of the pentane-1,5-diones (H) to the corresponding 4*H*-pyran (D) has been described.[117,131,145,163,176,177,179]

Despite the fact that, on treatment with acids, δ-diketones in general tend to undergo intramolecular aldol condensation with formation of cyclohexenone derivatives, γ-pyran derivatives are formed in many instances where this is allowed by structural factors. This reaction takes place on treatment with P_2O_5,[176] concentrated H_2SO_4,[163,173] and $ZnCl_2$,[131] but saturated carbaboranyl-1,5-diketones readily cyclise even at room temperature in acetic anhydride.[119,178,179]

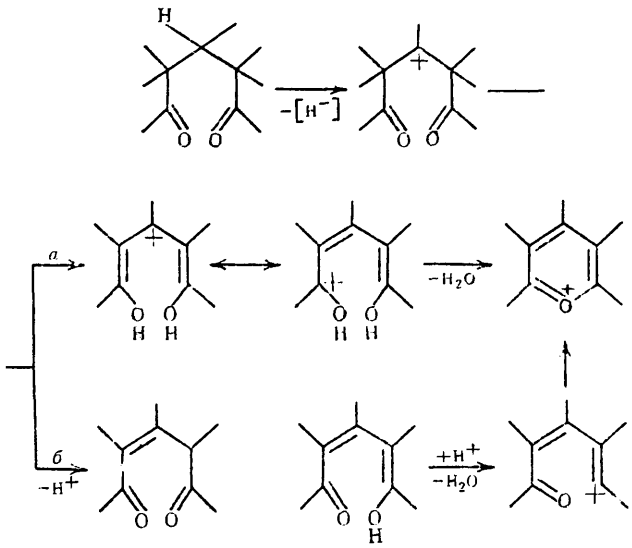
VII. SATURATED 1,5-DIKETONES–PYRYLIUM SALTS



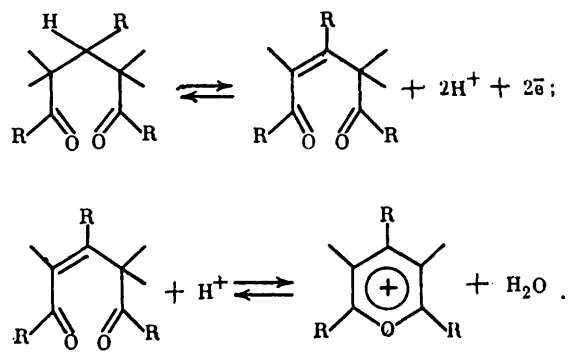
The conversion of saturated 1,5-diketones (H),[180,181] having a hydrogen atom at the C(3) atom, into pyrylium salts (A) is one of the most thoroughly investigated and most widely used methods of synthesis of pyrylium salts. An

¶ Analogous reactions are possible also for compounds (H') and (D') (Scheme 1).

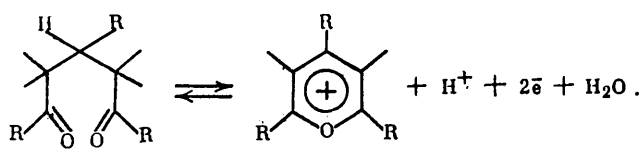
extensive compilation of the reagents used for this purpose has been published in reviews.[6,180] Since two processes take place in the course of thise reaction, namely dehydrogenation and dehydration, the question of the nature of the intermediate remained controversial for a long time. There were two hypotheses; according to the first, an unsaturated diketone is formed initially and then undergoes cyclodehydration to the pyrylium cation. It was assumed that ring closure after dehydrogenation is possible via both pathway *a* [182] and pathway *b*:[183,184]



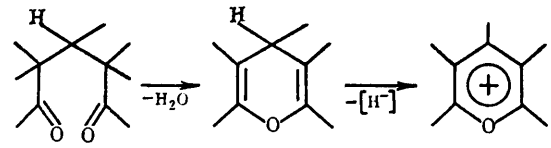
The study of the electrochemical oxidation potentials of saturated 1,5-diketones in acetonitrile using a rotating platinum electrode also led the authors[185] to the hypothesis of the initial formation of pentene-1,5-diones:



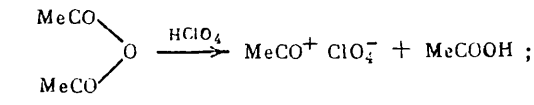
The overall process is

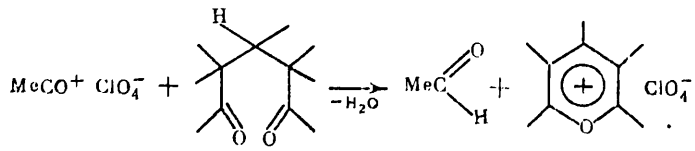


According to the second hypothesis, the initial stage in the formation of the pyrylium cation is the cyclodehydration of the 1,5-diketone with formation of a 4*H*-pyran, which is then converted into the pyrylium cation:



The abstraction of hydrogen was explained for a long time by the oxidising effect of the acid reagents. However, in the synthesis of pyrylium perchlorates in acetic anhydride, acetaldehyde was observed in the reaction mixture.[186] This finding permitted the hypothesis that organic carbonium ions, in particular that formed from acetyl perchlorate, may serve as hydride ion acceptors in salt formation†:





The supporters of the first hypothesis based their view on erroneous data showing that the cyclisation of 1,5-diketones to pyrans requires a strongly dehydrating medium[189] and also on the unsuccessful attempt to cyclise the saturated 1,5-diketone to a pyran with the aid of hydrobromic acid, which is a powerful protonating agent.[190] In the latter case one must bear in mind that the protonating medium promotes the reverse process involving the conversion of pyrans into diketones. Furthermore, there is no direct evidence for the formation of an unsaturated diketone from a saturated one and an indirect example illustrating the possibility of the dehydrogenation of an aliphatic straight chain by triphenylmethyl perchlorate is quoted in only one study,[189] the authors emphasing that it is unique.

On the other hand, it is fairly easy to split off water from a saturated 1,5-diketone with formation of 4*H*-pyrans; when carbonium ions are used, their dehydrating properties can be accounted for by the appearance of perchloric acid on interaction with acetic acid, in which most of the reactions are carried out:[191]

$$Ph_3CClO_4 + MeCOOH \rightarrow Ph_3COCOMe + HClO_4 .$$

Pyrylium salts have been synthesised[192] from a series of pentane-1,5-diones using trityl and acetyl cations in acetic anhydride, acetic acid, as well as their mixtures (in various proportions). It was shown that the joint action of trityl and acetyl cations is more effective than the action of each separately. On the basis of these experiments, it has been suggested that the pentanedione initially cyclises to a pyran, which is then dehydrogenated by triphenylmethyl perchlorate.

Concrete experimental evidence for the conversion of saturated 1,5-diketones into pyrylium salts via the formation of 4*H*-pyrans has been obtained recently. Thus, when penta-1,5-diones are treated with boron trifluoride etherate, 4*H*-pyrans are formed initially, their disproportionation subsequently resulting in the formation of pyrylium salts and tetrahydropyrans:[149]

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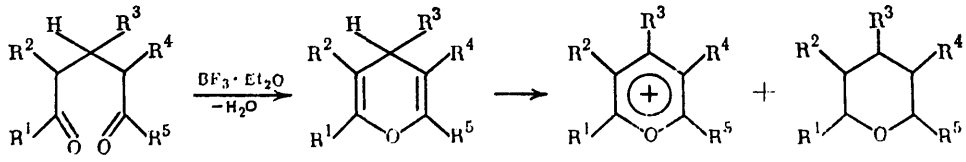
†The study of spectroscopic and solubility data for acyl perchlorates obtained from $AgClO_4$ and acid chlorides supports a covalent structure of the acetyl perchlorate $MeC(O)OClO_3$.[188]

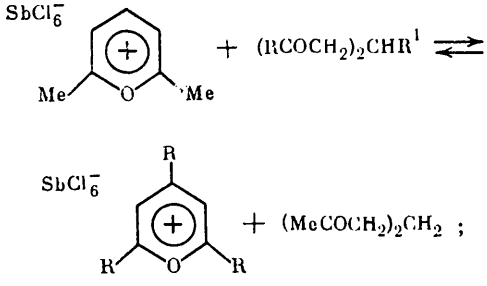


Boron trifluoride etherate apparently acts as a dehydrating agent in the first stage. This property of the trifluoride is well known.[193]

In addition, 3-carbaboranylpentane-1,5-diones are converted into 4*H*-pyrans in acetic anhydride, which acts as a dehydrating agent at room temperature.[119,178,179]

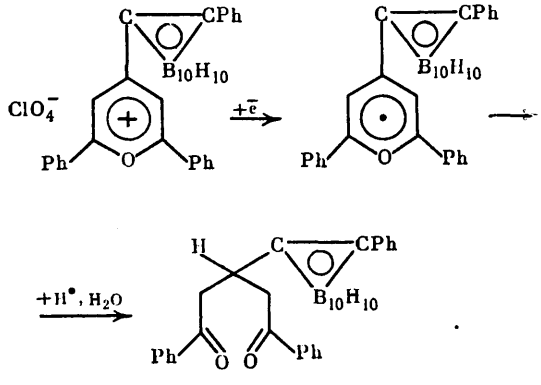
The above facts apparently make it possible to give preference to the formation of pyrylium salts from saturated 1,5-diketones via the 4*H*-pyran formation stage, as was done by a number of workers,[149,181,192,194] although it is so far difficult to give an unambiguous answer concerning the given mechanism, because the initial saturated 1,5-diketones themselves have different structures and the reaction media and the reagents employed are also varied.

Pyrylium salts can be converted in their turn into saturated 1,5-diketones. It has been shown[195] that the transfer of a hydride ion from the diketone to a less stable salt leads to the formation of a more stable salt and a new saturated 1,5-diketone:

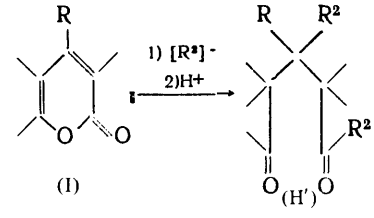


$R = R^1 = Ph$; $R = Ph$, $R^1 = H$.

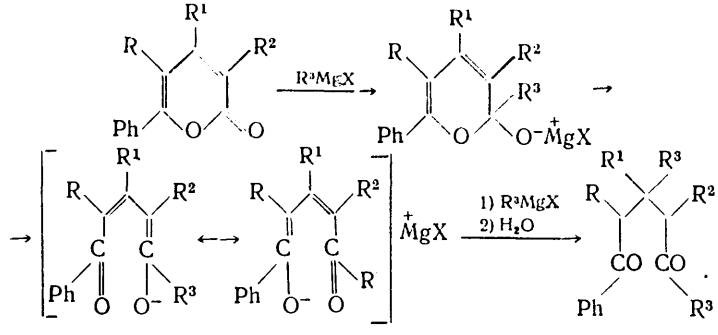
Pentene-1,5-diones are apparently formed from carbaboranylpyrylium salts via the stage in which a carbaboranylpyranyl radical is produced:[117,118]



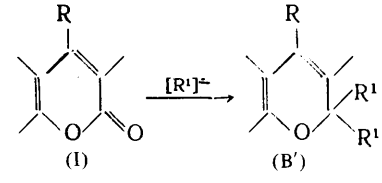
VIII. α-PYRONES–SATURATED 1,5-DIKETONES



When 2-pyrones (I)# are acted upon by Grignard reagents,[198–201] saturated 1,5-diketones (H′) may be formed. The interaction of phenylmagnesium bromide with α-pyrones containing the phenyl group in the 6-position, namely 6-phenyl-α-pyrone, 5-methyl-6-methyl-α-pyrone, and 3-methyl-6-phenyl-α-pyrone, leads exclusively to the formation of the corresponding pentane-1,5-diones in satisfactory yields.[199] In other cases saturated 1,5-diketones are formed together with keols, dienones, 2*H*-pyrans, etc. The reaction takes place via the following scheme:[199]

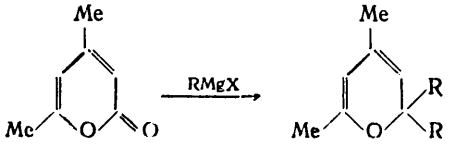


IX. α-PYRONES–2*H*-PYRANS

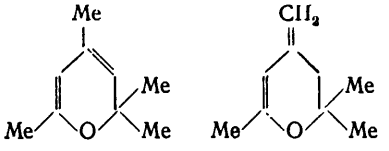


#Information about the methods of synthesis and properties of α-pyrones can be found in other reviews.[196,197]

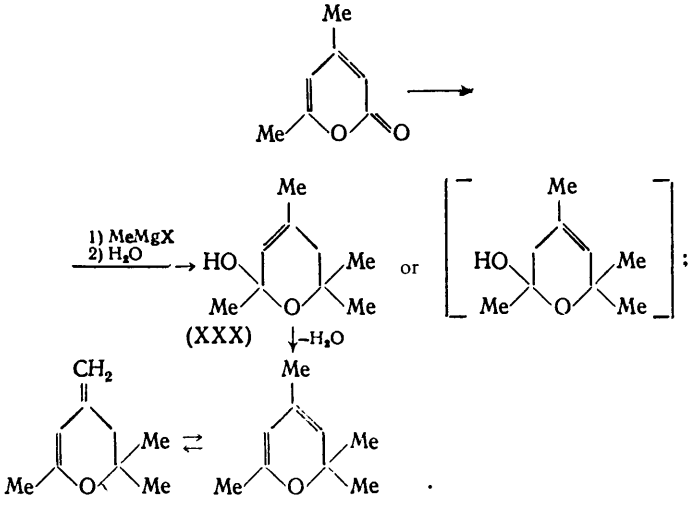
Treatment of α-pyrones with Grignard reagents is one of the main methods of synthesis of 2*H*-pyrans§.[32] The synthesis of 2*H*-pyrans by treating 2,4-dimethyl-α-pyrone with organomagnesium compounds was first reported by Gompper and Christmann:[202 203]



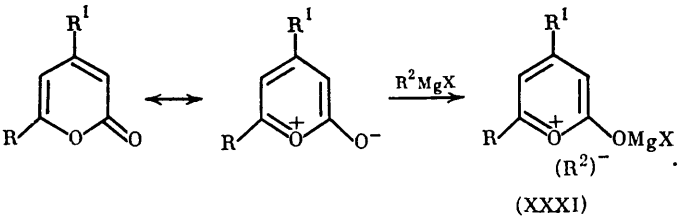
Repetition of this synthesis[204–210] showed that in the reaction involving methylmagnesium iodide, the products contained two isomers:



The isolation of the fairly unstable 6-hydroxy-2,2,4,6-tetramethyl-3,6-dihydro-2*H*-pyran (XXX) as an intermediate suggested the following mechanism of the above reaction:

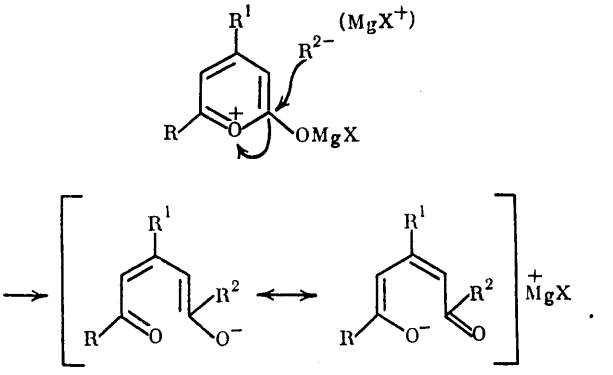


It is striking that, in the formation of 2*H*-pyrans by the reaction of α-pyrones with Grignard reagents, it is necessary to use a threefold excess [of the Grignard reagent], although it would appear that a twofold excess would have been sufficient according to the reaction stoichiometry. Experimental data showed that a complex of the pyrone with the Grignard reagent of type (XXXI) is formed initially¶:

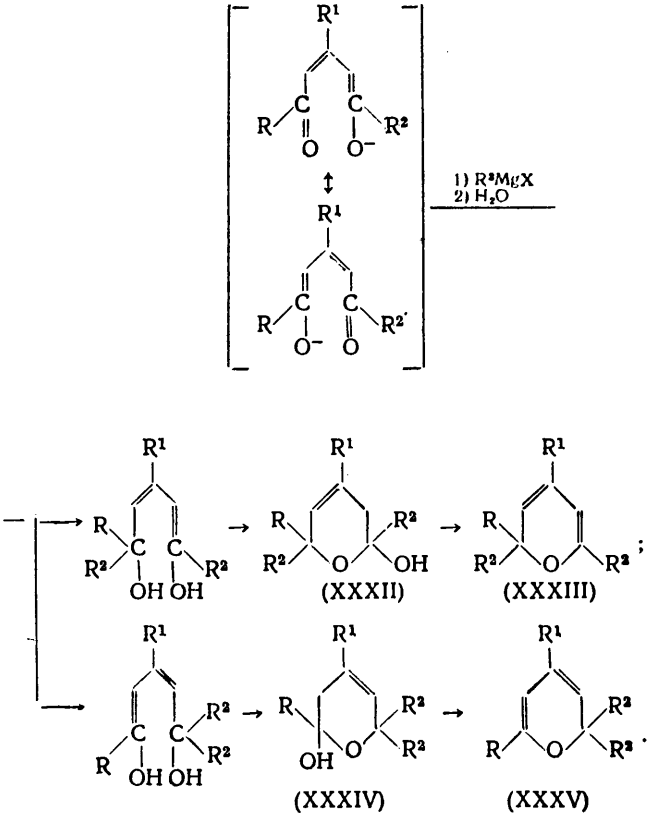


(XXXI)

On reaction with a second molecule of the alkylmagnesium halide, the ring opens with formation of the mesomeric enolate ion:



Finally, the enolate ion is attacked by a third molecule of the organomagnesium compound, which leads to two different 2*H*-pyrans—(XXXIII) and (XXXV):



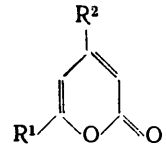
(XXXII) (XXXIII) (XXXIV) (XXXV)

§ The 2*H*-pyrans (B′) are capable of valence isomerisation to the *cis*-dienones (C′).

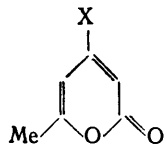
¶ The complex is a coloured compound, insoluble in ether, which decomposes during hydrolysis, occurring slowly even in an acid medium, with liberation of the initial α-pyrone.

It is striking that the dihydropyranols (XXXI) and (XXXIV) can be isolated only after hydrolysis in a neutral medium. After acid hydrolysis, the 2*H*-pyrans (XXXIII) and (XXXV) are formed.

The products of the interaction of the α-pyrones (XXXVI) and (XXXVII) with alkylmagnesium halides are 2*H*-pyrans as well as acyclic compounds: dienals, dienones, and saturated 1,5-diketones:[198]

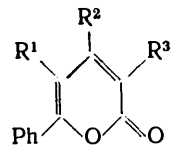


(XXXVI)
$R^1=R^2=H$; $R^1=H$, $R^2=Me$; $R^1=Me$, $R^2=Et$



(XXXVII)
X=OH, Cl, OMe .

The interaction of alkylmagnesium halides with α-pyrones (XXXVIII) containing the phenyl group in the 6-position has been investigated:[199]

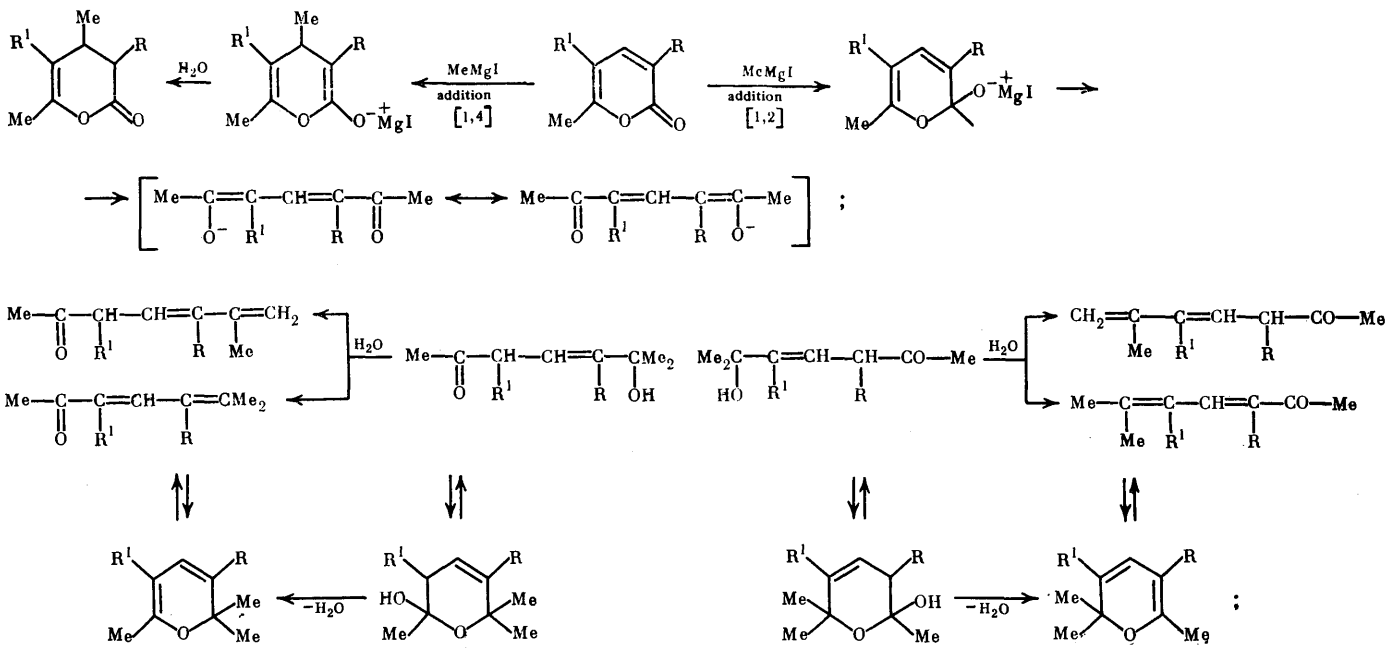


(XXXVIII)
$R^1=R^2=R^3=H$; $R^1=Me$, $R^2=R^3=H$; $R^1=R^3=H$, $R^2=Me$; $R^1=R^2=H$, $R^3=Me$; $R^1=R^3=H$, $R^2=Ph$.

Depending on the structure of the initial pyrone (XXXVIII), ketoenols, dienones, saturated 1,5-diketones, and dehydropyranols can be detected among the reaction products.

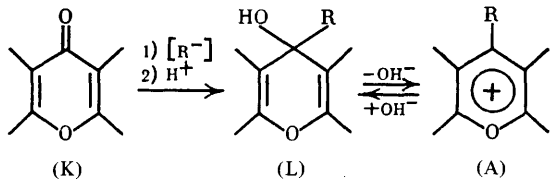
The study of the interaction of methylmagnesium iodide with α-pyrones unsubstituted in the 4-position[201,211] showed that 2*H*-pyrans can be obtained only from 3,5,6-trisubstituted derivatives. The 5,6-disubstituted α-pyrones give rise exclusively to compounds with a linear structure:

Scheme 2



R=R¹=Me; R=Ph, R¹=Me; R=H, R¹=Me; R=Me, R¹=H; R=H, R¹= *iso*-Pr; R=Ph, R¹=H; R=R¹=H

X. γ-PYRONES–γ-PYRANOLS–PYRYLIUM SALTS



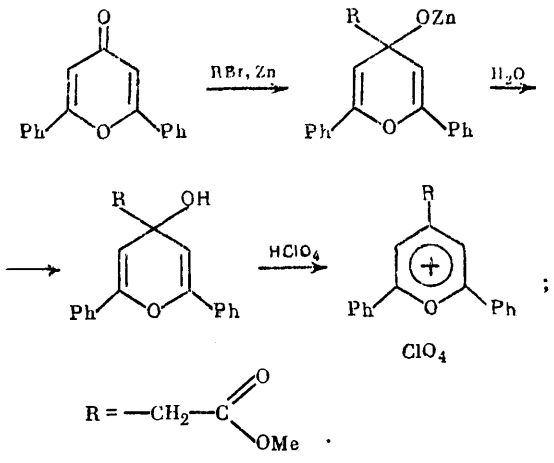
(K) (L) (A)

The γ-pyrones (K) are converted fairly readily into the γ-pyranols (L) and the latter are converted into pyrylium salts (A). The readily available 2,6-diphenyl- and 2,6-dialkyl-γ-pyrones therefore constitute a basis for the synthesis of a wide variety of pyrylium salts by interaction with organometallic compounds.

Thus the interactions of 2,6-dimethyl-γ-pyrones with methylmagnesium iodide and phenylmagnesium bromide yield respectively 2,4,6-trimethylpyrylium and 2,6-dimethyl-4-phenylpyrylium salts,[212] although Gomberg and Cone[213] and Elkaschef and Nossier[214] failed to observe a reaction between 2,6-dimethyl-γ-pyrone and phenylmagnesium bromide. There exist also other examples of the synthesis of pyrylium salts from γ-pyrones and organometallic compounds.[24,215,216]

It was assumed for a long time that the isolation of the intermediate γ-pyranols is impossible, although analogous compounds are known in the chromylium (benzopyrylium) and xanthylium series. It has been shown[109] that the alkoxides formed as a result of the interaction of γ-pyrones with organometallic compounds can be hydrolysed to γ-pyranols, which can be subsequently converted into pyrylium salts.

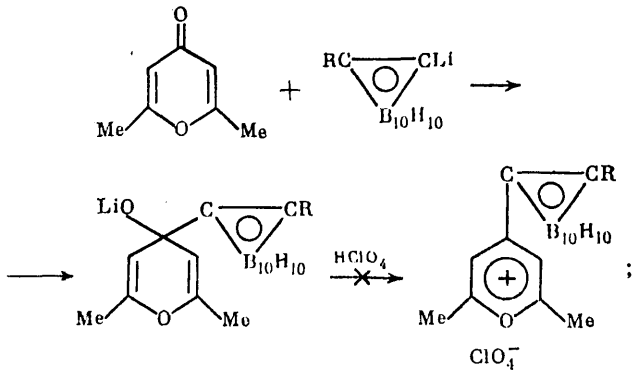
In recent years the range of organometallic compounds used in this reaction has been explained. For example, lithio-derivatives of the following heterocycles have been used: benzothiazole, pyridine, thiophen, and substituted furans.[108,109] 2,6-Diphenyl-γ-pyrone has been introduced into the Reformatskii reaction with formation of the methoxy-carbonylpyrylium cation:[217]



However, the authors were unable to extend this reaction to 2,6-dimethyl-γ-pyrone.

Indeed the reaction of γ-pyrones with organometallic compounds does not always proceed unambiguously. In particular, it has been noted[214] that the hydrolysis of the reaction mixture with dilute perchloric acid yields the pseudo-base and not the pyrylium salt.

After the interaction of 2,6-dimethyl-γ-pyrone with lithio-derivatives of *o*-carbaboranes, it was possible to isolate the intermediate lithium alkoxides derived from 2,6-dimethyl-4-R-*o*-carbaboranyl-γ-pyranols, which are precipitated during the reaction.[116,119] They are fairly stable high-melting point powders, although the alkoxides of tertiary carbaborane alcohols are usually unstable.[218] It was not possible to convert the alkoxides into the carbaboranyl-γ-pyranols on treatment with water or into pyrylium salts on treatment with perchloric acid:



R = H, Me, Ph.

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Another specific feature of six-membered oxygen-containing heterocycles, namely the tendency towards ring opening, has been strikingly manifested against the background of the intense investigations of the recyclisation of the heterocyclic systems.[11–14] The competition between two reaction pathways—recyclisation and ring opening—actually determines the character of the reactivity of these compounds.

The experimental and theoretical data accumulated hitherto enabled us to put forward a general mechanism for the reactions of six-membered oxygen-containing heterocycles (pyrylium salts, pyrans, and pyrones) and their open-chain forms, which, in our view, may be of definite assistance to synthetic chemists in selecting the method of synthesis of compounds belonging to the above classes or in the analysis of the structure of the substances formed in the course of the reactions indicated above. The data surveyed in this review are extremely useful for the elucidation of the following important problems in the chemistry of six-membered oxygen-containing heterocycles: the mechanism of the dehydroaromatisation of 4*H*-pyrans and the valence tautomerism of 2*H*-pyrans, the mode of reaction of α- and γ-pyrones with organometallic compounds, the structure of the pseudobases of pyrylium salts and the conditions governing their formation, the pathways leading to the conversion of saturated 1,5-diketones into pyrylium salts, etc. The series of studies by Katritzky and co-workers,[219–223] who investigated the kinetics of the opening of the rings of water-soluble

pyrylium salts in hydrolysis over a wide pH range and in ammonolysis by amines and who demonstrated the structure of the products by ^{1}H and ^{13}C NMR, is instructive in connection with the foregoing findings.

Questions concerning the opening of the pyran, pyrone, and pyrylium rings as a result of their coordination interaction with metal salts are of considerable interest. It is known that, in the complex of the 2*H*-pyran system with tungsten carbonyl, the ligand is fixed in the open-chain diene form;[224] this is not unexpected bearing in mind the high stability of this isomer in the non-coordinated state.[42,225] At the same time the formation of π-allyl complexes and the fixation of the open-chain forms of the ligands in the complexes of pyrylium salts with palladium(II) [226-229] and copper[230] indicate the possibility of using complex formation as an effective method for the opening of the rings in six-membered heterocycles and for the stabilisation, on coordination, of the isomers which are unusual for the free heterocycles.

Finally, we emphasise that the experimental and theoretical development of questions concerning the relative stabilities of the valence tautomers of oxygen-containing heterocycles makes it possible to identify the characteristic features of the steric and electronic structures which control the photochemical reactivity of the series of heterocyclic systems examined above[81,83,231] and assists in the search for the specific synthesis of photochromic systems with a specified set of properties.

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Fluorine-containing β-Ketoesters

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Data on the methods of synthesis, the keto-enol tautomerism, chemical properties, and applications of fluorine-containing β-ketoesters are surveyed. The characteristic features of these compounds due to the presence of fluorine atoms are specified. The bibliography includes 157 references.

CONTENTS

I. Introduction	1185
II. Methods of synthesis	1185
III. Structure and acidity	1187
IV. Chemical properties	1188
V. Applications	1197

I. INTRODUCTION

β-Ketoesters without fluorine (β-KE) have found applications in organic synthesis and industry. They are known as biologically active preparations and as extractants for many metals and they serve as the starting materials for the synthesis of a large number of compounds (metal chelates, ketones, and N- and S-containing heterocycles), which are also used in the national economy and in medicine. Effective and selective catalysts of polymerisation and polycondensation, pesticidal, antibacterial, antimalarial, and antiradiation preparations, and substances generating laser radiation have been found among β-KE derivatives. At the same time β-KE are of undoubted theoretical interest for the study of reactivity in relation to nucleophiles and electrophiles, tautomerism, and geometrical isomerism.

The introduction of fluorine atoms into β-KE alters their physicochemical properties, reactivity, biological activity, and other properties of practical and theoretical importance.

In many instances the presence of fluorine atoms in β-KE and their derivatives is responsible for the increase of their biological and catalytic activity and their resistance to corrosive media or leads to the appearance of new aspects of their applications. However, there have been no reviews of the literature data in this field of the chemistry of organofluorine compounds. Reviews have been published recently on fluorine-containing α-diketones and α-ketoesters [1] and β-diketones.[2] Some information about fluorine-containing β-KE (β-FKE) is available in monographs.[3-5]

The aim of the present review is to survey the literature data on the synthesis, properties, and applications of β-FKE and to compare them with those of their hydrocarbon analogues, which makes it possible to discover the features due to the presence of fluorine atoms in β-KE. The review covers the literature up to 1983 inclusive.

II. METHODS OF SYNTHESIS

The first fluorine-containing β-KE, namely trifluoroacetoacetic ester (TFAAE) was obtained by Swarts[6] by the Claisen condensation in 1926.[6] In 1929 difluoroacetoacetic ester was obtained by the same method.[7]

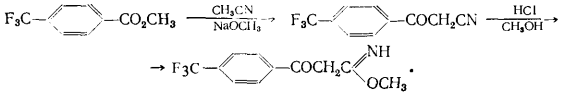
It has been shown[8] that the condensation of the methyl esters of difluoro- or trifluoroacetic acid with ethyl acetate in ether using equimolar proportions of the reactants in the presence of sodioethylene leads to the corresponding β-FKE in moderate yields (35 and 54% respectively). A method for the purification of β-FKE via copper chelates is described in the same communication. A β-KE with the heptafluoropropyl group has been obtained analogously:[9]

$$R_FCO_2C_2H_5 + CH_3CO_2C_2H_5 \xrightarrow[\text{ether}]{C_2H_5ONa} R_FCOCH_2CO_2C_2H_5;$$
$$R_F = HCF_2\ (35\%),\ CF_3\ (54\%)\ [8];\ C_3F_7\ (90\%)\ [9].$$

Acetoacetic ester (AAE) is formed by this method from ethyl acetate in 75% yield.[10] The condensation of ethyl monofluoroacetate with formic acid ester makes it possible to obtain the α-fluoro-substituted β-aldoester:[11]

$$CH_2FCO_2C_2H_5 \xrightarrow[C_2H_5ONa]{HCO_2C_2H_5} HCOCHFCO_2C_2H_5.$$

The self-condensation of monofluoroacetic ester in the presence of sodium alkoxides affords α,γ-difluoroacetoacetic ester in 23% yield.[12,13] Treatment of monofluoroacetic ester under these conditions with acetyl chloride leads to α-fluoroacetoacetic ester in 10% yield.[14] The ester of trifluoromethylbenzoic acid reacts with acetonitrile to form a β-ketonitrile whose alcoholysis makes it possible to obtain a β-ketoiminoester:[15]



The use of sodium alkoxides as condensing agents for the synthesis of β-FKE is not always effective. Thus the self-condensation of difluoroacetic ester and its reaction with trifluoroacetic ester do not lead to β-FKE on treatment with sodium alkoxides in ether,[8] although the use of sodium hydride makes it possible to obtain β-FKE containing one or two fluorine atoms in the α-position in 20–86% yields.[16,17] β-FKE with the pentafluoroethyl residue has also been synthesised by this method:[14,18]

$$C_2F_5CO_2C_2H_5 + XCH_2CO_2C_2H_5 \xrightarrow[\text{ether}]{NaH} C_2F_5COCHXCO_2C_2H_5;$$
$$X = H\ (87\%),\ F\ (70\%)\ [14].$$

t-Butyl 4,4,4-trifluoro-3-oxobutanoate and ethyl 4,4,4-trifluoro-2-methyl-3-oxobutanoate have been obtained in the same way in 56 and 50% yields.[18] 2,2,2-Trifluoroethyl formylphenylacetate is formed under analogous conditions from trifluoroethyl phenylacetate and trifluoroethyl formate:[19]

$$C_6H_5CH_2CO_2CH_2CF_3 \xrightarrow[NaH]{HCO_2CH_2CF_3} \underset{\displaystyle C_6H_5\ 46\%}{\overset{\displaystyle |}{HCOCHCO_2CH_2CF_3}}.$$

Monofluoroacetic ester reacts with t-butyl methyl ketone in the presence of sodium hydride in ether to form α,γ-difluoroacetoacetic ester.[20] Acetyl chloride and benzoyl chloride

condense with monofluoroacetic ester on treatment with sodium hydride.[14] Both the α-fluoro-derivative of AAE and a diketoester, which is a product of the acylation of the α,γ-difluoro-derivative, are formed in the first case:

$$CH_2FCO_2C_2H_5 \xrightarrow[NaH,\ ether]{C_6H_5COCl} C_6H_5COCHFCO_2C_2H_5;\ 30\%$$

$$CH_2FCO_2C_2H_5 \xrightarrow[NaH,\ ether]{CH_3COCl} CH_3COCHFCO_2C_2H_5 + CH_2FCOC(COCH_3)CO_2C_2H_5.$$

When metallic sodium is used as the condensing agent, TFAAE is formed in 77% yield;[21] trifluoroacetic ester and diethyl succinate give rise to an α-ethoxycarbonyl-substituted β-FKE in the presence of sodium:[22]

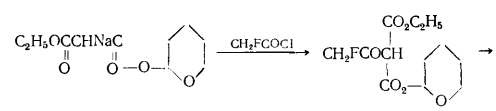
$$CF_3CO_2C_2H_5 \xrightarrow[Na,\ 80°]{(CH_2CO_2C_2H_5)_2} CF_3COCH(CH_2CO_2C_2H_5)CO_2C_2H_5.$$

It is of interest that treatment of trifluoroacetic ester with sodium in liquid nitrogen does not produce pentafluoroacetic ester but gives rise to TFAAE and sodium fluoride.[23] The abstraction of fluorine atoms has been confirmed in the preparation of TFAAE on treating pentafluoroacetoacetic ester with sodium in ether:[23]

$$CF_3CO_2C_2H_5 \xrightarrow[-NaF]{Na} [CF_2{=}C(ONa)OC_2H_5] \xrightarrow{CF_3CO_2C_2H_5} \{CF_3COCF_2CO_2C_2H_5\} \xrightarrow[-NaF]{Na} CF_3COCH_2CO_2C_2H_5 \xleftarrow[-NaF]{Na} CF_3COCF_2CO_2C_2H_5.$$

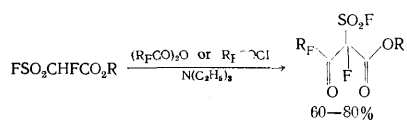
Hydrogen is probably abstracted from the solvent by the intermediate carbonium ion.

Triphenylmethylsodium was used in the condensation of trifluoroacetic ester with isobutyric ester.[17] γ-Fluoroacetoacetic ester has been obtained by acylating the sodium derivative of ethyl tetrahydropyranyl malonate with thermal decomposition of the product:[24]



$$\xrightarrow[-CO_2]{\Delta} CH_2FCOCH_2CO_2C_2H_5.$$

A convenient method of synthesis of the β-FKE with the fluorosulphonyl group in the α-position has been developed recently. It consists in the acylation of esters of fluorosulphonylfluoroacetic acid by the anhydrides or chlorides of carboxylic fluoroacids in the presence of triethylamine:[25]



60—80%

R = CH_3, iso-C_3H_7; R_F=CF_3, CF_2CF_2H, C_3F_7, C_4F_9, C_6F_{13}.

The synthesis of monofluoro- and difluoro-derivatives of β-KE by the condensation of halogen-containing esters in the presence of magnesium and mercury chloride in ether (in yields of 19—52%) has been described:[14]

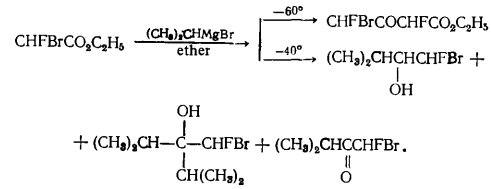
$$R^1CO_2C_2H_5 \xrightarrow[Mg,\ HgCl_2]{R^2CHXCO_2C_2H_5} R^1COCHR^2CO_2C_2H_5;$$

$R^1 = CH_2F$, X = Br, R^2=H(20%); R^1=CH_2F, X=Cl, R^2=H;
R^1=CH_2F, X=Br, R^2=CH_3 (19%); R^1=CH_3, X=Cl, R^2=F (20%);
R^1=CHFCl, X=Cl, R^2=F (52%).

Sterically hindered esters of bromine-containing carboxylic acids can also be involved in this reaction in the presence of zinc in benzene:[26]

$$C_2H_5CHFCO_2C_2H_5 \xrightarrow[Zn,\ C_6H_6]{(CH_3)_2CBrCO_2C_2H_5} C_2H_5CHFCO(CH_3)_2CO_2C_2H_5.$$

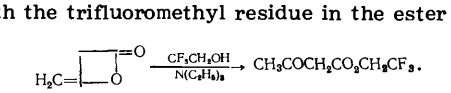
On treatment with isopropylmagnesium bromide, ethyl bromofluoroacetate gives rise to substituted β-KE at −60 °C in ether, whereas at −40 °C a mixture of alcohols and a ketone is formed:[27]



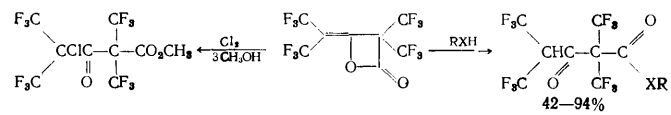
The interaction of keten and its derivatives with acid chlorides and alcohols yields β-KE which are difficult to obtain by other methods. Keten reacts with trifluoroethanol and trichloroacetyl chloride to form in a high yield β-FKE containing the trichloro- and trifluoro-methyl groups:[28]

$$CH_2{=}C{=}O + CCl_3COCl \xrightarrow[SO_2]{CF_3CH_2OH} CCl_3COCH_2CO_2CH_2CF_3.\ 79\%$$

The keten dimer reacts with trifluoroethanol to produce a β-FKE with the trifluoromethyl residue in the ester group:[29]



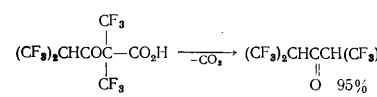
The cyclic dimer of perfluorodimethylketen forms a whole series of trifluoromethyl-substituted β-KE and their derivatives in reactions with HO-, HS-, and N-nucleophiles.[30,31] When the perfluorodimethylketen dimer is chlorinated in the presence of methanol, coupled addition takes place with formation of a γ-chloro-substituted β-FKE. In the absence of methanol, the reaction does not take place:[31]



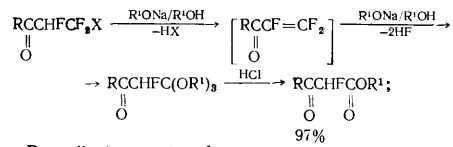
42—94%

X = O, S, or NH; R = H, alkyl, or phenyl.

The interaction of the perfluorodimethylketen dimer with water affords a β-ketoacid which is unstable at room temperature:[31]



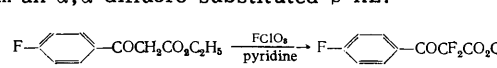
The method of synthesis of α-fluoro-substituted β-FKE involving the treatment of unsaturated fluoroketones with sodium alkoxides and subsequent acid hydrolysis of the products of the vinyl substitution of fluorine and addition to the double bond is apparently promising:[32,33]



97%

R = alkyl or aryl; R^1 = CH_3, C_2H_5; X=F, Cl.

A number of methods of synthesis of β-FKE are based on the introduction of halogen atoms into the β-KE molecule. *p*-Fluorobenzoylacetic ester reacts with perchloryl fluoride to form an α,α-difluoro-substituted β-KE:[34]



A similar reaction takes place in alcohol in the presence of sodium ethoxide.[35,36] A fluorine atom can be introduced into the isopropyl group of the β-KE when isobutyric acid ester reacts with triphenylmethylsodium and perchloryl fluoride:[37]

$$(CH_3)_2CHCO_2CH_3 \xrightarrow[(C_6H_5)_3CNa]{FClO_3} (CH_3)_2CFCOCCO_2CH_3 \quad (30\%)$$

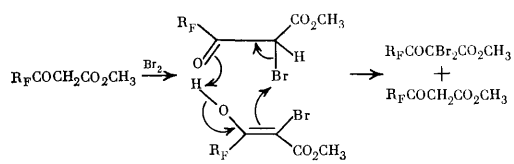
The chlorination of β-FKE or their copper chelates gives rise to α-chloro-derivatives:[38-40]

$$R_FCOCH_2CO_2R \xrightarrow[20^\circ]{Cl_2} R_FCOCHClCO_2R \xleftarrow[CHCl_3]{Cl_2} [R_FCOCHCO_2R]_2Cu;$$
$$R_F=CF_3,\ H(CF_2)_n,\ n=1,\ 2,\ 4;\ C_3F_7,\ C_4F_9;\ R=CH_3,\ C_2H_5.$$

α-Chloro-derivatives of aromatic β-FKE with fluorine-containing substituents in the aromatic ring have been synthesised also by treatment with sulphuryl chloride in chloroform (in yields of 80–90%).[41] Treatment of TFAAE with bromine in a chloroform–pyridine mixture leads to a dibromo-substituted β-KE:[40,42]

$$CF_3COCH_2CO_2C_2H_5 \xrightarrow[CHCl_3,\text{pyridine}]{Br_2} CF_3COCBr_2CO_2C_2H_5.$$

However, when an attempt was made to synthesise α-monobromo-derivatives of β-FKE by treating them with bromine, as described for α-bromotrifluoroacetoacetic ester,[39,43] it was found that they are relatively unstable.[43] At room temperature or on vacuum distillation their disproportionation to α,α-dibromo-derivatives and the initial β-FKE is observed, apparently owing to the halogenophilic attack by the enol form of the α-bromo-derivative of the β-FKE on the bromine atom of the keto-form:



$R_F = CF_3,\ H(CF_2)_n,\ C_4F_9;\ n = 1, 2, 4.$

A second halogen atom can be introduced into the α-position in the β-KE by brominating the α-fluoro-derivative:[44]

$$CF_3COCHFCO_2C_2H_5 \xrightarrow[CCl_4,\ 70^\circ]{Br_2} CF_3COCFBrCO_2C_2H_5.$$

A β-FKE containing an aromatic polyfluoro-group can be synthesised by acylating malonic ester with the chloride of pentafluorobenzoic acid with subsequent hydrolysis and decarboxylation of the acylation product or by the condensation of pentafluorobenzoic ester with ethyl acetate in the presence of diisopropylaminomagnesium bromide:[45-47]

$$C_6F_5COCl \xrightarrow[MgBr(OC_2H_5)]{CH_2(CO_2C_2H_5)_2} C_6F_5COCH(CO_2C_2H_5)_2 \xrightarrow[H_2O]{H_2SO_4}$$
$$C_6F_5CO_2C_2H_5 \xrightarrow[(iso\text{-}C_3H_7)_2NMgBr]{CH_2CO_2C_2H_5} C_6F_5COCH_2CO_2C_2H_5.$$

The same compound was formed on oxidation of the β-hydroxyester, obtained by the Reformatskii reaction, with chromium trioxide or potassium permanganate:[47]

$$C_6F_5C(=O)H \xrightarrow[Zn]{BrCH_2CO_2C_2H_5} C_6F_5CH(OH)CH_2CO_2C_2H_5 \xrightarrow{CrO_3}$$
$$\rightarrow C_6F_5COCH_2CO_2C_2H_5 + C_6F_5COCH_3 + C_6F_5CO_2H.$$
$$17\%$$

The first two methods of synthesis of pentafluorobenzoylacetic ester (PFBAE) are preferable because they lead to higher yields.

Thus one may conclude that the most universal and most convenient, as regards yields, purity of the reaction products, and the availability of the initial reagents, method of synthesis of a wide range of aliphatic β-FKE is the Claisen condensation. As for β-diketones,[2] the most convenient and most widely used method of purification of β-FKE involves the formation of copper chelates.

III. STRUCTURE AND ACIDITY

A whole series of monographs and reviews have been devoted to problems of the structure of β-dicarbonyl compounds,[48-50] but they are concerned mainly with β-KE without fluorine. Data obtained from studies of β-FKE by electronic absorption spectroscopy are virtually lacking in the literature and the available experimental absorption maxima and extinction coefficients are quoted mainly as characteristics of the given substances. The results obtained by Filler and Naqvi[51] permit the conclusion that the replacement of all three hydrogen atoms of the methyl group in AAE by fluorine atoms entails a hypsochromic shift of the absorption maximum (λ_{max} = 244 and 234 nm respectively in 2,2,4-trimethylpentane). For copper chelates of β-KE, such a shift has not been observed; on passing from AAE chelates of TFAAE chelates, there is almost no change in the position of the absorption band maxima in the ultraviolet spectra (278 and 276 nm in chloroform).[51]

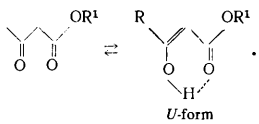
Table 1. Infrared spectra of β-KE [ν(cm^{-1}) in CCl_4].

Compound	Keto-form		Enolic form			Refs.
	>C=O	–C(=O)OR		>C=C<	–OH	
$CH_3COCH_2CO_2C_2H_5$	1715	1740	1645	1625	—	[28]
$CH_3ClCOCH_2CO_2C_2H_5$	1726	1745	1656	1632	—	[28]
$CCl_3COCH_2CO_2C_2H_5$	1767	1741	1662	1626	—	[28]
$CCl_3COCH_2CO_2CH_2CF_3$	1755	1777	1683	1627	—	[28]
$CH_2FCOCH_2CO_2C_2H_5$	1730	1745	1660	1635	—	[51]
$CHF_2COCH_2CO_2C_2H_5$	1765	1745	1670	—	3125,3565	[51]
$CF_3COCH_2CO_2C_2H_5$	1775	1740	1670	1640	—	[51]
Ditto	1775	1750	1680	—	3400,3965	[28]
$(CF_3)_2CHCOCCO_2CH_3^*$ (CF$_3$)	1783	1755	—	—	—	[30]
$C_3F_5COCH_2CO_2C_2H_5$	1748	—	1656	—	—	[47]

*Without solvent.

Application of infrared (IR) spectroscopy to the study of the structures of halogen-containing β-KE revealed the presence of the keto- and enol forms. Table 1 shows that the reducton of halogen atoms (Cl and F) increases the absorption frequencies of the keto-groups in both the keto- and enol forms. This tendency has also been observed for the absorption by the C=C bond in the enolic forms of β-KE. In most studies it has been noted that acetoacid esters form

enols with the *U*-conformation (a *cis,cis*-enol with an intramolecular hydrogen bond):[48,50]



U-form

Table 2. The enolisation β-KE (pure liquids, ^{1}H NMR).

Compound	K_e^* (Ref.55)	Content of enol, %	References
$CH_3COCH_2CO_2C_2H_5$	0.087	6—8	[52—54]
Ditto	—	7.7***	[56]
$CH_3BrCOCH_2CO_2C_2H_5$	—	6	[52]
$CH_2FCOCH_2CO_2C_2H_5$	0.22	7.2	[53]
Ditto	—	18.2***	[56]
$CHF_2COCH_2CO_2C_2H_5$	1.13	53	[53]
$CF_3COCH_2CO_2C_2H_5$	5.7	89	[52,53]
Ditto	—	49***	[56]
$CF_3COCH(CH_3)CO_2C_2H_5$	0.9	—	—
$CF_3COCH(C_6H_5)CO_2C_2H_5$	1.4	—	—
$CF_3COCH(OCH_3)CO_2C_2H_5$	3.0	—	—
$CF_3COCH(C_3H_7)CO_2C_2H_5$	0.22	—	—
$CF_3COCH(C_3H_7\text{-iso})CO_2C_2H_5$	0.003	—	—
$CH_3COCHBrCO_2C_2H_5$	—	5	[50]
$CH_3COCHClCO_2C_2H_5$	—	15	[50]
$CH_2ClCOCHClCO_2C_2H_5$	0.158	—	—
$CH_3COCHFCO_2C_2H_5$	0.158	15	[50]
Ditto	—	0.99***	[56]
$CCl_3COCH_2CO_2CH_2CF_3$	—	21.2	[28]
$HCOCH(C_6H_5)CO_2CH_2CF_3$	—	54	[19]
$C_6F_5COCH_2CO_2C_2H_5$	1.17	54	[47]
$C_6H_5COCH_2CO_2C_2H_5$	0.28**	20	[47]

*K_e = [enol]/[ketone].
**Filler et al.[47]
***Data obtained by the method involving titration with bromine.[56]

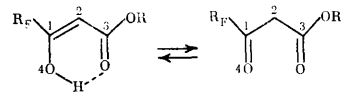
The methods for the investigation of the keto–enol equilibria involving β-KE which are most convenient and yield most information are IR and NMR spectroscopy.[19,47,50,52–55] Data for the enolisation of β-KE, obtained by titration with bromine,[56] agree satisfactorily with the results obtained by other methods (Table 2) only for β-KE without halogens. In the case of fluorine-containing β-KE they are clearly erroneous, in all probability owing to the uncertainty as to the course followed in the bromination process.[40] Table 2 shows that the introduction of halogen atoms into the α- and γ-positions in β-KE entails a sharp increase of the enol content in the equilibrium mixture, which may be attributed to a greater increase in the CH acidity than the OH acidity. The β-KE are enolised only at the carbonyl oxygen atom.[50] The lower degree of enolisation of β-KE compared with β-diketones[2,50] is in all probability associated with the greater electron density on the carbon atom of the carbonyl group owing to the presence of alkoxy-groups. The contribution of the influence of γ-substituents in the enolic forms of β-KE to the intramolecular hydrogen bond is not additive, in contrast to β-diketones.[57]

The charges on the atoms and the bond energies in the keto- and enol forms of a series of α- and γ-fluoro-substituted β-KE have been calculated[55] by Del Re's method. Correlations between the keto-enol equilibrum constants ($\lg K_e$) and the parameters of the reaction centres have been investigated. A linear relation has been observed ($r = 0.995$, $\alpha = 0.95$) between $\lg K_e$ and the charges on the β-carbon atoms in the keto and enol forms of β-KE and on the hydrogen atom of the enolic hydroxyl and also the O–H bond energy of the enol.[55]

The acidity of β-FKE has been investigated by Kurts et al.,[58] who established that the introduction of fluorine atoms into the γ-position in β-KE increases their activity, in conformity with the inductive effect of the substituents [AAE: $pK_a = 12.6$; γ-F-AAE: $pK_a = 11.2$; TFAAE: $pK_a = 7.4$ (in dimethylformamide)]; consequently the stability of the enolate ion increases under these conditions. One can also note that, on passing from β-KE to the corresponding β-diketones (replacement of OC_2H_5 by CH_3), the acidity increases [acetylacetone: $pK_a = 11.7$; trifluoroacetylacetone: $pK_a = 5.1$ (in dimethylformamide)], which also agrees with the inductive effect of the substituents.

IV. CHEMICAL PROPERTIES

Fluorine-containing β-ketoesters have four reaction centres: C(1), C(2), C(3), and O(4):



This is the reason for their varied reactivity in relation to nucleophiles and electrophiles. The introduction of fluorine atoms increases the reactivity in relation to nucleophiles and in many cases alters the reaction mechanisms compared with their hydrocarbon analogues. The presence of the ester group leads to the appearance of chemical properties uncharacteristic of fluorine-containing β-ketones.

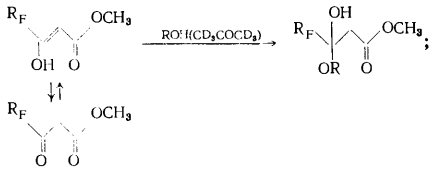
1. Interaction with Nucleophiles

HO, HS, HN, and other nucleophiles react with β-FKE, forming addition and addition-elimination products from which one can infer the characteristic features of substances of this class. In the study of reactions of the given type, the question of the direction of the primary processes, namely either via the C(1) carbon atom in the keto- or enol form or via the C(3) atom (the ester group), is significant. However, one cannot rule out the process involving the formation of a salt of the enol form. Thus the reactions of β-FKE with nucleophiles must be regarded as competing interactions with the C(1), C(2), and C(3) reaction centres. Naturally one must also take into account the influence of the medium.

(a) Reactions with Hydroxylated Nucleophiles

In the absence of a solvent, TFAAE combines with water and alcohol, forming hydrates and hemiketals, which are in equilibrium with keto- and enol forms.[59] Since the enolisation constant K_e, determined by ^{19}F NMR, increases after the addition of water to TFAAE, the authors of the above study concluded that the addition is to the keto-form and that the reaction is faster than the attainment of the keto–enol equilibrium. However, in another study by the ^{1}H and ^{19}F NMR methods, of the interaction of β-FKE with water and alcohols in deuterioacetone, it was shown that they add to the

enol form of β-FKE and that K_e diminishes with time:[60]

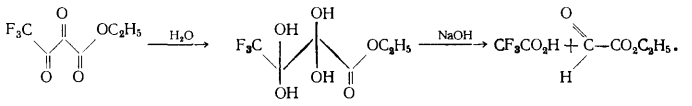


R_F=H(CF_2)$_n$, (n = 1, 2, 4), CF_3, C_3F_7, C_4F_9, R=H, CH_3, C_2H_5.

The discrepancy between the results obtained cannot be accounted for by the influence of the solvent (CD_3COCD_3), since in the case of asymmetric fluorine-containing β-diketones, hydroxylated nucleophiles also added to the enol form, the content of the keto-form hardly changing under these conditions, while the solvent (CD_3COCD_3) does not influence the reaction mechanism.[61] The results of the study of Camps et al.[59] cannot be interpreted in detail because of the inadequacy of the experimental data presented. Furthermore, the use of the analysis of the [enol]/[ketone] ratio is not quite correct, since there are no data concerning the influence of alcohols on the keto–enol equilibria of β-FKE.

An increase in the length of the fluoroalkyl group (from difluoromethyl to nonafluorobutyl) in β-FKE and also the increase of the bulk of the alkyl substituents in the hydroxylated nucleophile lead to a decrease of the fraction of the adduct, which is in all probability associated with steric hindrance.[60] It is of interest that butyl 2,2,4,4,4-pentafluoroacetoacetate reacts with butanol to form a stable adduct, which can be isolated pure, this being due to the appreciable decrease of the electron density at the C(1) centre compared with TFAAE as a result of the replacement of the methylene group by the difluoromethylene group.[16] It is clearly seen from the data of Burdett and Rogers[52] and Fomin et al.[60] that the introduction of the trifluoromethyl group in AAE instead of the methyl group entails an increase in the reactivity and stability of the products of the addition of hydroxylated nucleophiles compared with AAE, for which the formation of large amounts of adducts is not a characteristic feature. On heating PFBAE with aqueous alcohol, the ester undergoes keto cleavage to pentafluoroacetophenone, which has not been observed for benzoylacetic ester (BAE).[62]

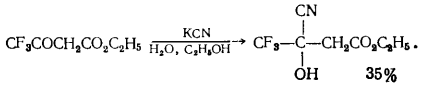
Trifluoro-α-oxoacetoacetic ester reacts with water to form a dihydrate, while in its reaction with aqueous alkali it undergoes acid cleavage:[63,64]



Thus the interaction of β-FKE containing fluoroalkyl groups in the β-position with hydroxylated nucleophiles, including the hydroxide anion, is directed to the C(1) centre. The ketone cleavage of PFBAE in a water–alcohol mixture is apparently associated with its low thermal stability.

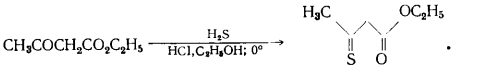
(b) Interaction with C-Nucleophiles

TFAAE reacts with potassium cyanide[65,66] to form a cyanohydrin analogously to the behaviour of carbonyl compounds without fluorine atoms:[10]

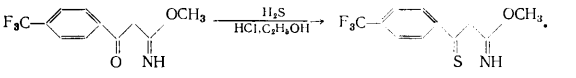


(c) Interaction with HS-Nucleophiles

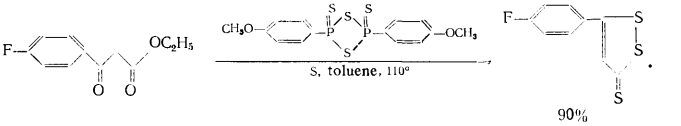
AAE reacts with hydrogen sulphide to form thioacetoacetic esters:[67]



A similar reaction of TFAAE has not so far been described. Only thio-derivatives of aromatic β-KE with the trifluoromethyl substituent in the benzene ring have been obtained:[15]



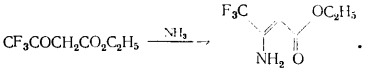
On interaction with *p*-fluorobenzoylacetic ester, the "*p*-methoxyphenylthionophosphine sulphide dimer", which is an effective thionating agent, gives rise to only a cyclic disulphide, as for AAE:[68]



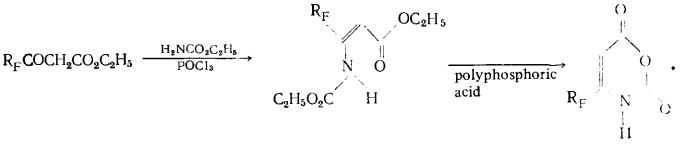
Thioesters cannot be isolated in this instance. The mechanism of the interaction of this reagent with β-KE is still obscure. This branch of the chemistry of β-FKE has remained virtually uninvestigated, while in the case of fluorine-containing β-diketones it has been adequately developed.[2]

(d) Interaction with Amines

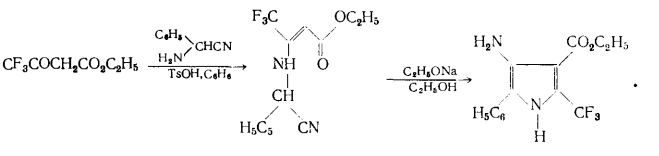
The interaction of AAE with ammonia leads to ethyl β-aminocrotonate in 90% yield.[69] TFAAE also reacts with ammonia to form β-aminotrifluorocrotonic ester:[6,70,71]



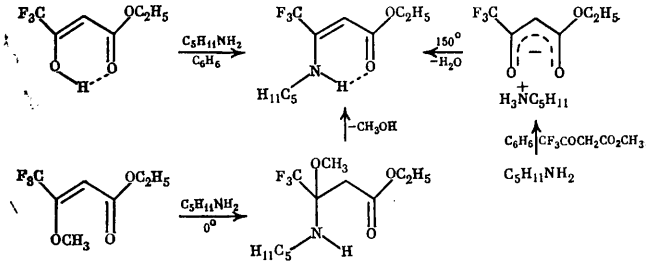
Fluoro- and trifluoro-acetoacetic esters react with urethane in the presence of phosphoryl chloride, forming esters of *N*-substituted-aminocrotonic acids, which cyclise to oxazinediones on treatment with polyphosphoric acid;[72] AAE condenses immediately to oxazinedione,[22] which can apparently be accounted for by the fact that in the case of fluorine-containing compounds the reactivity of the enamine formed is reduced in relation to electrophiles owing to the presence of electron-accepting groups (CH_2F, CF_3):



The interaction of TFAAE with α-aminophenylacetonitrile in the presence of toluene-*p*-sulphonic acid in benzene gives rise to a derivative of aminotrifluorocrotonic acid, from which a substituted pyrrole is formed on treatment with sodium ethoxide in ethanol:[73]

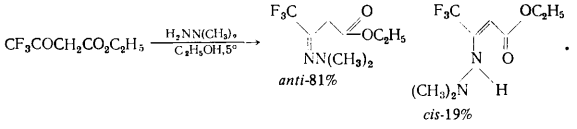


Analogous products have been obtained from AAE and *p*-fluorobenzoylacetic ester.[73] It has been shown that, depending on the order of the addition of the reactants, the interaction of TFAAE with pentylamine leads either to 4,4,4-trifluoro-3-(1-pentylamino)but-2-enoate or to the pentylammonium salt of TFAAE, which is converted into an enamine with elimination of water at 150 °C.[18] Presumably the enolic form of the β-ketoester reacts with the amine, since trifluoro-β-methoxycrotonic ester reacts with pentylamine to form initially a relatively unstable adduct which splits off methanol and is converted into 4,4,4-trifluoro-3-(1-pentylamino)but-2-enoate:[18]



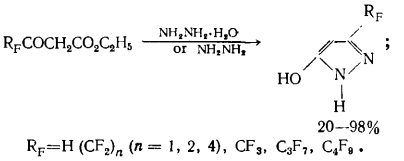
(e) Interaction with Hydrazines

TFAAE reacts with asymmetric *NN*-dimethylhydrazine to give a 62% yield of a hydrazone, which exists, according to ^{1}H NMR data, in the form of an equilibrium mixture of the *anti*-hydrazone form (81%) and the *cis*-enehydrazine form (19%):[74]



Under analogous conditions, the corresponding AAE hydrazone exists as a mixture of the hydrazone form (15% of the *syn*-isomer and 10% of the *anti*-isomer) with the enehydrazine form (72% of the *cis*-isomer and 3% of the *trans*-isomer).[74]

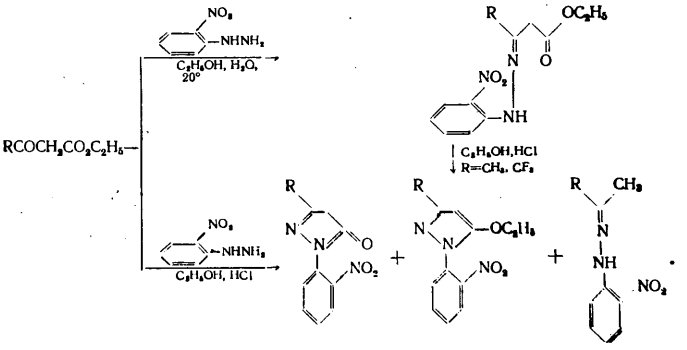
TFAAE andother β-FKE react with hydrazine hydrate or hydrazine to form 5(3)-fluoroalkyl-3(5)-hydroxypyrazoles:[75–77]



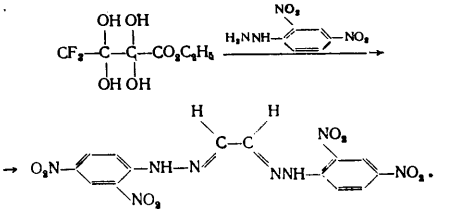
R_F=H $(CF_2)_n$ (n = 1, 2, 4), CF_3, C_3F_7, C_4F_9.

β-KE monosubstituted by fluorine in the α-position also give rise to hydroxypyrazoles.[78]

β-FKE react with phenylhydrazine and methanol at 20 °C to form *N*-phenylhydrazones, which cyclise to 5-fluoroalkyl-3-hydroxy-*N*-phenylpyrazoles on refluxing in methanol.[77] The formation of hydrazone has been noted in the reaction of γ-fluoroacetoacetic ester with 2,4-dinitrophenylhydrazine [24] and of TFAAE with 2-nitrophenylhydrazine.[79] However, as a rule oxo- or hydroxy-pyrazoles are formed in the reactions of β-FKE with hydrazines.[75–77,80,81] A more detailed study of this process in relation to the reaction of AAE or TFAAE with 2-nitrophenylhydrazine showed that the results depend to a large extent on the experimental conditions.[79] Thus the products in aqueous alcohol at 20 °C are arylhydrazones, which, on treatment with alcoholic hydrogen chloride, afford a mixture of pyrazolone, ethoxypyrazole, and the hydrazone of the corresponding methyl ketone, formed apparently on ketone cleavage of the β-KE, whereas in alcohol containing hydrogen chloride the above mixture of products is formed immediately:[79]



On treatment with 2,4-dinitrophenylhydrazine, the dihydrate of trifluoro-2-oxoacetoacetic ester decomposes with formation of glyoxal bis-2,4-dinitrophenylhydrazone:[64]

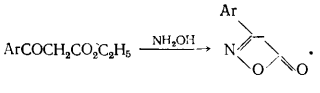


In the reactions of β-FKE with pentafluorophenyl groups in the β-position with hydrazine[62] and phenyl- and pentafluorophenylhydrazines,[82] the corresponding pyrazolones are formed. On the other hand, BAE reacts with pentafluorophenylhydrazine to form the pentafluorophenylhydrazone;[82] cyclisation to a pyrazolone is not observed in this case, apparently as a consequence of the insufficient nucleophilicity of the nitrogen in the HN groups of the hydrazone. At the same time, the pentafluorophenylhydrazone of PFBAE cyclises spontaneously to the pyrazolone, which is in all probability due to the electrophilic properties of the carbon atom in the ethoxycarbonyl group enhanced under the influence of the pentafluorophenyl residue.

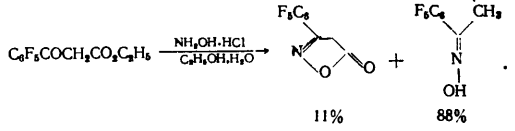
According to IR spectroscopic data, pyrazolones containing one or two pentafluorophenyl substituents consist in the solid state of a mixture of the hydroxy-form with a small amount of the keto-form, while 1,3-diphenyl-5-pyrazolone exists under these conditions as the keto-form.[82] In alcoholic solutions these pyrazolones exist in the enolic-form, while in carbon tetrachloride or in methylene chloride they are present predominantly in the keto-form.[82] It follows from the above that, in the interaction of hydrazines with β-FKE, the primary attack by the hydrazine is directed to the C(1) carbon atom, which is indicated by the formation of hydrazones in certain cases, the interaction involving the C(3) reaction centre and cyclisation to pyrazolones only under more severe conditions.[77,79]

(f) Interaction with Hydroxylamine

The *para*- and *meta*-trifluoromethyl derivatives of PAE react with hydroxylamine to form isoxazolones:[83–85]



Pentafluorobenzoylacetic ester reacts with hydroxylamine to form a salt and not an isoxazolone, which can be explained by its high acidity.[82] However, when PFBAE is heated with hydroxylamine hydrochloride in aqueous alcohol, 3-pentafluorophenyl-5-isoxazolone is obtained together with pentafluoroacetophenone oxime:[62]

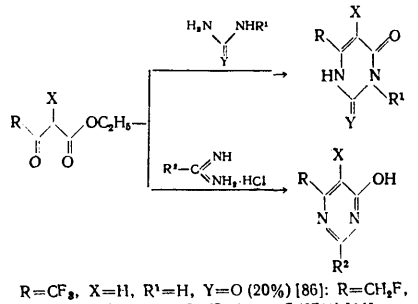


11% 88%

The formation of the oxime agrees well with the fact that, on heating in aqueous alcohol, PFBAE undergoes ketone cleavage to pentafluoroacetophenone, whose reaction with hydroxylamine affords the oxime.[62]

(g) Interaction with Ureas, Guanidine, Semicarbazides, and Amidines

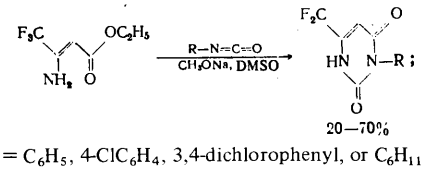
The interaction of β-FKE with ureas[14,86-88] in basic[86] or acid[14] media, with thiourea in the presence of sodium methoxide,[14] with guanidine carbonate,[14] and with carboxylic acid amidines[14-89] leads to uracils, thiouracils, isocytosines, and hydroxypyrimidines substituted in the 2-position respectively:



R=CF_3, X=H, R¹=H, Y=O (20%) [86]; R=CH_2F, X=H, R¹=H, Y=O (73%) or S (67%) [14]; R=CH_3, X=F, R¹=Ar, Y=O [87, 88];

R=CH_3, CH_2F, CF_3 or C_2F_5, X=H or F, R¹=H, Y=NH·H_2CO_3 [14]; R=CH_3, CH_2F, CF_3 or C_2F_5, X = H or F, R^2 = CH_3 or iso-C_3H_7 [14, 89].

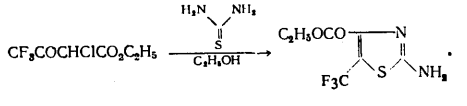
Fluorine-containing uracils are formed also from β-aminocrotonic esters and isocyanates:[71, 90]



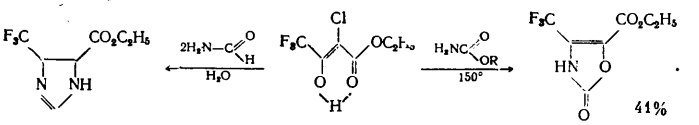
20–70%

R = C_6H_5, 4-ClC_6H_4, 3,4-dichlorophenyl, or C_6H_{11}.

If there is a chlorine atom, which is more mobile than the fluorine atom, in the α-position in β-FKE, then the reaction follows another pathway: the ethyl ester of 2-amino-4-trifluoromethylthiazolecarboxylic acid is formed on interaction with thiourea:[41,91]



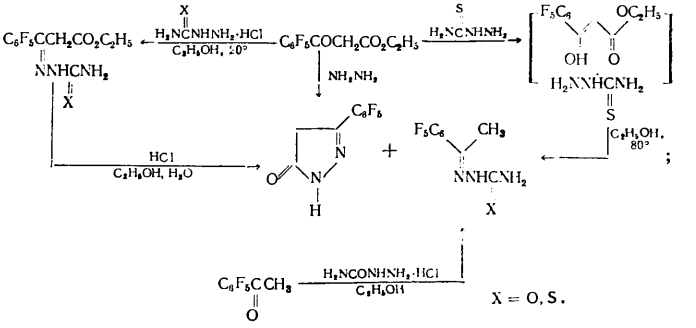
The mobility of the chlorine atom in the α-position in β-FKE is also manifested in the interaction of the chloro-substituted TFAAE with formamide or urethane:[92,93]



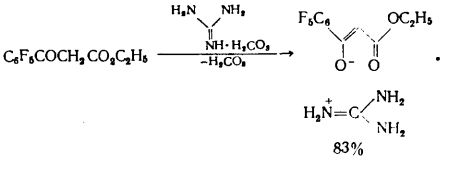
41%

The interaction of PFBAE with semicarbazide hydrochloride or thiosemicarbazide hydrochloride at 20–25 °C involves the C(1) reaction centre.[62] On heating, the PFBAE derivative undergoes the ketone cleavage and the semicarbazone residue decomposes to the hydrazone residue, so that a derivative of pentafluoroacetophenone is obtained together with pentafluorophenylpyrazolone.[62] The reaction with thiosemicarbazide gives rise not to the thiosemicarbazone but to an unstable salt, which is converted on heating into the same products as thiosemicarbazide hydrochloride.[62]

The presence of 3-pentafluorophenyl-5-pyrazolone in the products of the reaction of PFBAE with semicarbazide can be accounted for by the partial decomposition of the latter to hydrazine.[62,95] Its structure has been demonstrated by specific synthesis from a β-FKE and hydrazine:[62]



The formation of a salt with thiosemicarbazide is extremely probable, since the guanidinium salt of the enolic form of PFBAE has been isolated in the reaction with guanidine carbonate:[82]



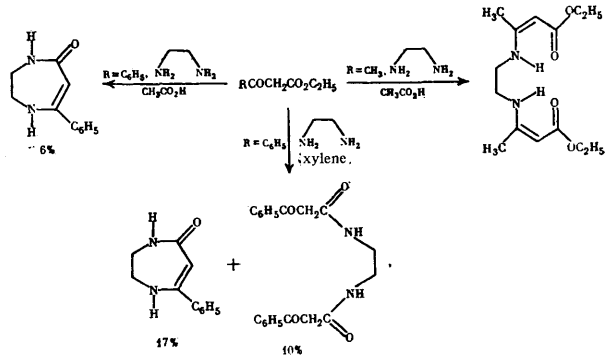
83%

In this case BAE gives rise to 4-phenylisocytosine.[94] This can be explained by the increased acidity and degree of enolisation of PFBAE compared with BAE.[47]

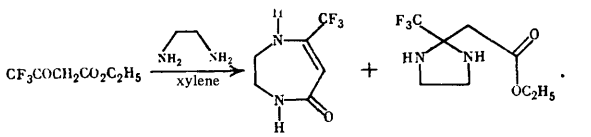
(h) Reactions with Bifunctional Nucleophiles

The interaction of AAE with ethylenediamine (EDA) in acetic acid does not give rise to an azepinone, but produces *NN'*-ethylenebis-3-amino-but-2-enoate.[96] However BAE does form 7-phenyl-1,2,3,4-tetrahydro-1,4-diazepin-5-one under

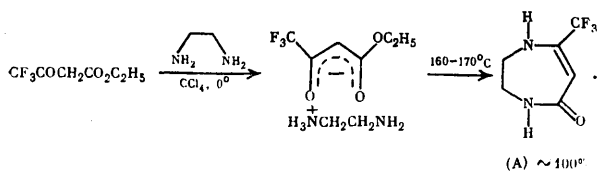
these conditions, while in xylene *NN'*-ethylenebisbenzoylacetamide is obtained in addition;[96]



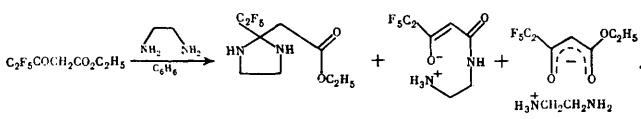
In contrast to this, the reaction of TFAAE with EDA in xylene affords a mixture of 7-trifluoromethyl-1,2,3,4-tetrahydro-1,4-diazepin-5-one (A) and 2-ethoxycarbonylmethyl-2-trifluoromethylimidazolidine (B):[97]



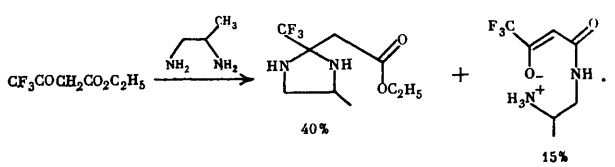
When TFAAE was added to EDA in boiling benzene, 36% of compound (B) and 10% of compound (A) were obtained while in ethanol only the product (B) was formed in 19% yield. On the other hand, after the addition of EDA in TFAAE, compound (B) was obtained in 81% yield, while the diazepine (A) was not isolated.[18] The addition of EDA to a solution of TFAAE in carbon tetrachloride results in the formation of the ethylenediammonium salt of TFAAF, which is converted quantitatively into the diazepinone (A) on heating:[18]



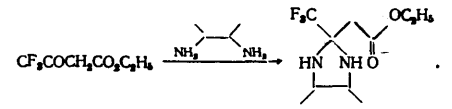
The addition of EDA to a boiling benzene solution of ethyl 4,4,5,5,5-pentafluoro-3-oxopentanoate produces 2-ethoxycarbonylmethyl-2-perfluoroethylimidazolidine, *N*-(2-aminoethyl)-3-hydroxy-4,4,5,5,5-pentafluoropent-2-enamide, and the ethylenediammonium salt of the β-FKE:[18]



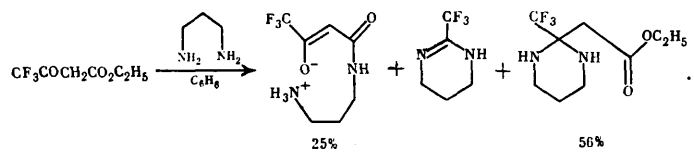
The addition of TFAAE to 1,2-diaminopropane in benzene results in a mixture of the *d*- and *l*-isomers of a substituted imidazolidine together with *N*-(2-aminepropyl)-3-hydroxy-4,4,4-trifluorobut-2-enamide, which gives rise to 2-methyl-7-trifluoromethyl-1,2,3,4-tetrahydro-1,4-diazepin-5-one on heating:[18]



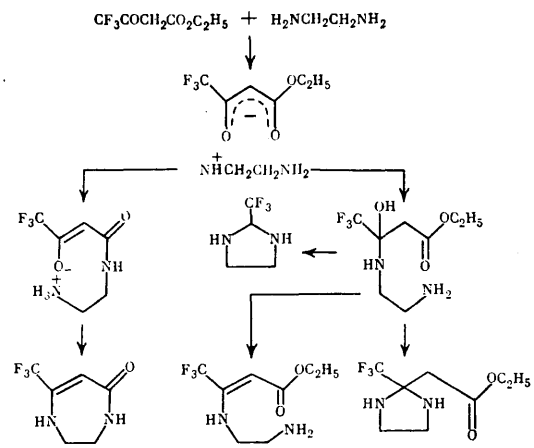
The reaction of TFAAE with 2,3-diaminobutane produces a mixture of the *d*-, *l*-, and *meso*-isomers of a substituted imidazolidine:[18]



The reaction of 1,3-diaminopropane with TFAAE leads to *N*-(3-aminopropyl)-3-hydroxy-4,4,4-trifluorobut-2-enamide, 2-trifluoromethyl-3,4,5,6-tetrahydropyrimidine, and 2-ethoxycarbonylmethyl-2-trifluoromethylhexahydropyrimidine:[18]



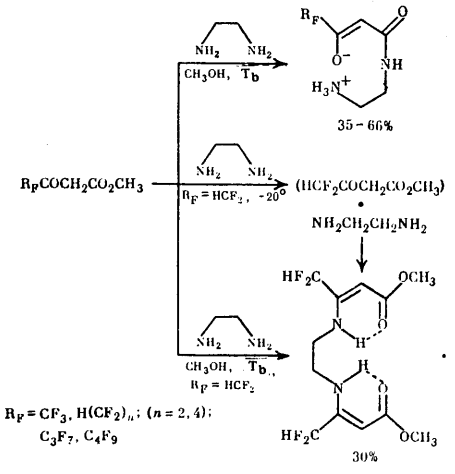
From the above data, the following mechanism of the reaction of TFAAE with EDA in aprotic solvents has been proposed:



As can be seen from the above scheme, the authors[18] suggest the presence of two competing pathways in the reaction of the TFAAE salt with EDA: the formation of an adduct via the C(1) centre with subsequent dehydration and the substitution of the ethoxy-group in the ester group of TFAAE [attack on the C(3) centre].

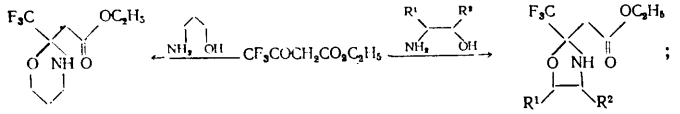
The replacement of an aprotic solvent by a proton-donating solvent (methanol) entails an appreciable simplification of the composition of the products of the reaction of β-FKE with EDA.[77] Thus, when difluoroacetoacetic ester is refluxed with EDA in methanol, 3,3'-(*NN'*-diaminoethylene)bis-1,1-difluorobut-2-enoate is formed,[77] which is also characteristic of AAE,[96] while at −20 °C it is possible to isolate a 2:1 salt of difluoroacetoacetic ester with EDA, which is converted on heating into the same dicarboxylic acid ester.[77] The replacement of the difluoromethyl group by the trifluoromethyl group or the lengthening of the fluoroalkyl residue results in the formation of an inner salt of the aminoethyleneamide of the β-ketoacid as the sole reaction

product:[77]



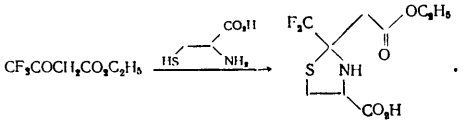
Apparently the primary process in the interaction of EDA with β-FKE in a proton-donating solvent[77] is, as in an aprotic solvent,[18] the formation of a salt of the β-FKE. However, the subsequent reaction pathway is apparently determined by the acidity of the β-FKE and, in the case where R_F = HCF_2, the reaction involving the C(1) centre (a carbonyl group) takes place, whereas under conditions where R_F has been lengthened the reaction involves the C(3) centre (the ester group).

TFAAE reacts with aminoalcohols to form 2-ethoxycarbonylmethyl-2-trifluoromethylperhydroxooxazine or the corresponding oxazolidine:[18]

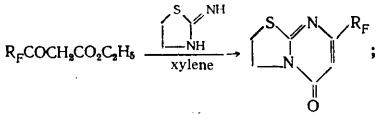


R¹=R²=H; R¹=CH₃, R²=H; R¹=H, R²=CH₃.

Cysteine reacts with TFAAE to form 4-carboxy-2-ethoxycarbonylmethyl-2-trifluoromethylthiazolidine:[18]

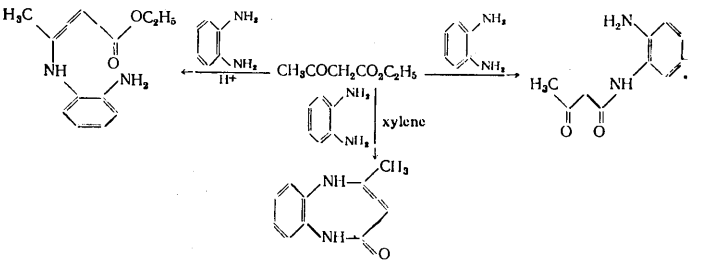


These reactions also show that the attack by the HO-, HN-, and HS-nucleophiles is directed to the C(1) centre, although in the case of the HN-nucleophiles this can be preceded by the formation of a salt with the β-FKE. 2-Iminothiazolidine reacts with β-FKE to form thiazolinopyrimidine derivatives:[98]

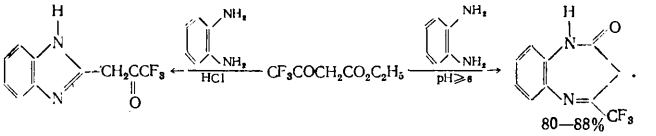


R_F = CF_3, *m*-$CF_3C_6H_4$.

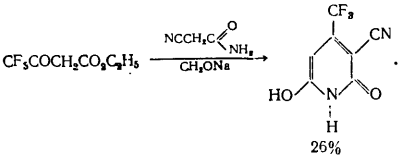
The reaction of AAE with *o*-phenylenediamine (OPDA) results in the formation of various products depending on the basicity of the medium and the character of the solvent.[99–111] In an acid medium the product of the condensation involving a keto-group is formed, in xylene containing pyridine the *o*-aminoanilide is obtained, while in a neutral medium the product is a substituted benzodiazepinone:[100]



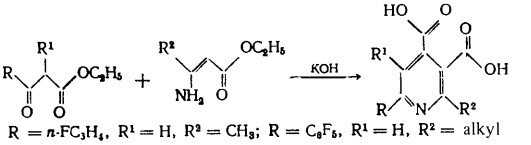
However, there exist data showing that these processes are more complex.[99,101] For example, in methanol 2-methylbenzimidazole was isolated together with a derivative of β-aminocrotonic ester.[101] The interaction of TFAAE and other β-FKE with OPDA in a neutral or weakly alkaline medium entails the formation of 4-(fluoroalkyl)-1*H*-1,5-benzodiazepin-2(3*H*)-ones,[77] while in an acid medium the product is 3-(2-benzimidazolyl)-1,1,1-trifluoro-2-propanone:[102]



Methyl-*o*-phenylenediamine reacts with TFAAE to produce a mixture of two isomers.[103] β-FKE react with bifunctional nucleophiles containing an active methylene group together with the amino-, hydroxy-, or thio-groups, which leads to different heterocyclic systems.[104–118] Thus the reaction of TFAAE with cyanoacetamide gives rise to a substituted pyridone;[104]

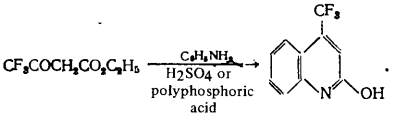


Under the influence of alkali, β-FKE react with β-aminocrotonic esters to form derivatives of dibasic acids of the pyridine series,[105] which is also characteristic of AAE:[106]



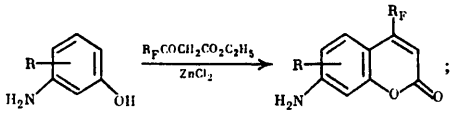
R = *n*-FC_3H_4, R^1 = H, R^2 = CH_3; R = C_6F_5, R^1 = H, R^2 = alkyl

Like AAE,[10] TFAAE reacts with aniline and its derivatives in the presence of sulphuric or polyphosphoric acid to form hydroxyquinolines and their derivatives.[107–113] The yields of the reaction products are then as a rule higher in the case of polyphosphoric acids:[108–110]



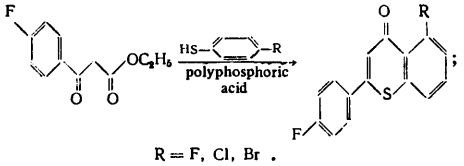
Like the fluorine-free β-KE,[10] β-FKE react with aromatic dihydric phenols and aminophenols via the hydroxy-group and the *ortho*-position in the ring, forming coumarins in

20–80% yields:[114–117]



$R_F = CF_3, C_3F_7, C_5F_{11}, C_7F_{15}$; R = OH, NH_2, $C_6H_5CH_2$— .

Thiophenols react with β-FKE via the S–H and –CH= groups:[118]



R = F, Cl, Br .

The considerable synthetic possibilities of the reactions of β-FKE with nucleophiles, which makes it possible to obtain various classes of fluorine-containing organic compounds, are evident from the foregoing data for these reactions; their characteristic features, which distinguish them from their hydrocarbon analogues, must also be emphasised.

2. Interaction with Electrophiles

The reactions with electrophiles, namely acids,[8,16,22,34,39,44,47,119] carbonyl compounds,[126–129] and alkylating and acylating agents[51,119,143,144] (see Section II about the halogenation of β-FKE) are characteristic of β-FKE, as in the case of their hydrocarbon analogues.

(a) Reactions with Acids

Fluorine-containing β-ketoesters having a fluoroalkyl substituent in the β-position and not more than one fluorine atom in the α-position undergo the ketone cleavage by sulphuric[8,16,44] or hydrobromic[39] acid with formation of fluoroalkylmethyl, fluoroalkylhalogenomethyl, or fluoroalkyldihalogenomethyl ketones in high yields (50–90%):

$$R_FCOCXYCO_2C_2H_5 \xrightarrow[-CO_2,\ -C_2H_5OH]{H^+} R_FCOCHXY;$$
R_F = fluoroalkyl; X = H, F, Cl, Br; Y = H, Br .

In the presence of two fluorine atoms in the α-position in β-FKE acid hydrolysis of the ester group, leading to β-keto acids, is observed under similar conditions and not the ketone cleavage:[16]

$$CF_2XCOCF_2CO_2C_2H_5 \xrightarrow[-C_2H_5OH]{H_2SO_4} CF_2XCOCF_2CO_2H;$$
X = H (53%), F (56%).

Ketone cleavage takes place only under more severe conditions, giving rise to 1,1,3,3-tetrafluoroacetone (62%) in the first case and 1,1,1,3,3-pentafluoroacetone (35%) in the second case.[16] Treatment of a β-KE having the $CH_2CO_2C_2H_5$ substituent in the α-position with sulphuric acid makes it possible to obtain a γ-ketoacid:[22]

$$CF_2COCHCO_2C_2H_5 \xrightarrow[-CO_2,\ -C_2H_5OH]{H_2SO_4} CF_2COCH_2CH_2CO_2H.$$
61%

Treatment of β-FKE mono- and di-substituted in the α-position with a mixture of bromine and sulphuric acid makes it possible to obtain di- and tri-halogeno-substituted methyl ketones respectively:[44]

$$CF_2COCFXCO_2C_2H_5 \xrightarrow[-CO_2,\ -C_2H_5OH]{Br_2,\ H_2SO_4} CF_2COCFXBr;$$
X = H (95%), Br (84%).

In contrast to fluoroalkyl-containing β-FKE, on treatment with concentrated sulphuric acid PFBAE hydrolyses at 20 °C to pentafluorobenzoylacetic acid, while on treatment with 20% sulphuric acid or a mixture of sulphuric and acetic acids it is cleaved to pentafluoroacetophenone:[47,82]

$$C_6F_5COCH_2CO_2H \xleftarrow{H_2SO_4\ (conc.)} C_6F_5COCH_2CO_2C_2H_5 \xrightarrow[\text{or } H_2SO_4\text{–}CH_3CO_2H]{20\%\ H_2SO_4} C_6F_5COCH_3.$$
48%

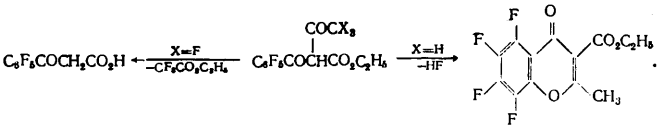
α-Ethoxycarbonylpentafluorobenzoylacetic ester reacts with 10% sulphuric acid to form PFBAE:[47]

$$C_6F_5COCHCO_2C_2H_5 \xrightarrow{10\%\ H_2SO_4} C_6F_5COCH_2CO_2C_2H_5.$$
48%

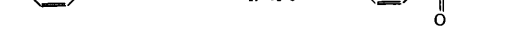
The ketone cleavage of β-FKE with benzoyl, pentafluorobenzoyl and pentafluorophenylacetyl substituents in the α-position is a convenient method of synthesising β-diketones with one or two pentafluorophenyl groups:[119]

$$C_6F_5COCHCO_2C_2H_5 \xrightarrow[-CO_2,\ -C_2H_5OH]{H_2SO_4(conc.)} C_6F_5COCH_2COR;$$
R = C_6H_5, C_6F_5 (78%), $CH_2C_6F_5$ (77%).

However, when the acetyl group is present in the α-position, a substituted flavone is formed, while in the presence of the trifluoroacyl substituent pentafluorobenzoylacetic acid is obtained.[119] The formation of the flavone can be explained by the cyclisation of the initial β-FKE owing to the intramolecular substitution of the *ortho*-fluorine atom in the pentafluorobenzene ring and the formation of pentafluorobenzoylacetic acid can be accounted for by the fact that in this case the α-ethoxycarbonyl-β-diketone undergoes acid and not keton cleavage:



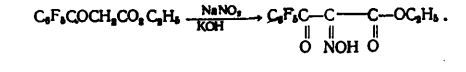
α,α-Difluoro-substituted *p*-fluorobenzoylacetic ester reacts with a mixture of hydrochloric acid and acetic acid to form the corresponding substituted benzophenone:[34]



Thus the majority of β-FKE are converted into ketones on interaction with acids. The first stage of this reaction is the acid hydrolysis of the ester group to the β-ketoacid, which is then decarboxylated to the ketone.

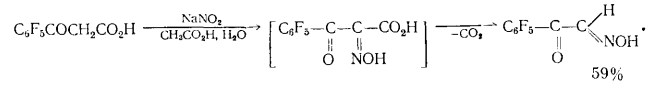
(b) Nitrosation and Diazotisation

These reactions are known only for β-FKE with the pentafluorophenyl group.[82,120] Treatment of PFBAE with sodium nitrite is accompanied by the formation of pentafluoroisonitrosobenzoylacetic ester:[82,120]



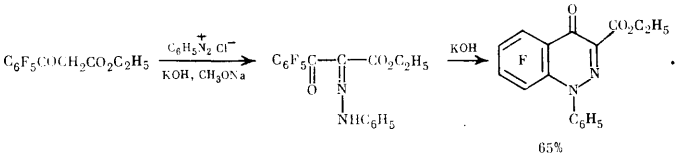
In contrast to this, pentafluorobenzoylacetic acid reacts with sodium nitrite in an acid medium to form the oxime of pentafluorophenylglyoxal, which is in all probability the

product of the decomposition of the intermediate pentafluoroisonitrosobenzoylacetic acid:[120]



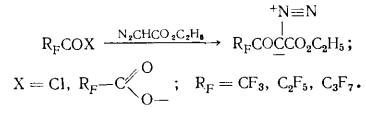
59%

The reaction of PFBAE with benzenediazonium chloride in an alkaline medium gives rise to a cinnolinone derivative:[82]

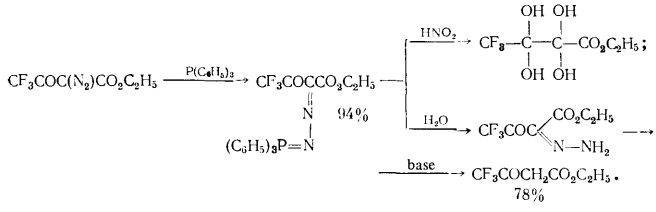


65%

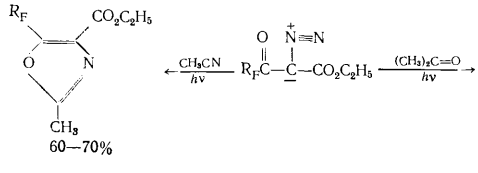
Here we should mention the α-diazo-derivatives of β-FKE, although they are not products of the reactions of β-FKE and are formed as a rule from diazoacetic ester and the chlorides or anhydrides of carboxylic fluoroacids:[64,121,122]



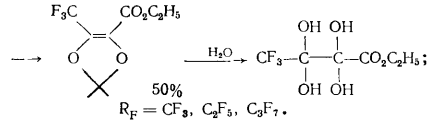
Numerous β-FKE can be obtained from these compounds.[43,64,121–125] α-Diazotrifluoroacetoacetic ester reacts with triphenylphosphine to form a product whose treatment with water gives rise to a compound with the structure of a hydrazone; the hydrolysis of the latter in a basic medium produces TFAAE.[121] However, when the product is treated with nitrous acid in tetrahydrofuran and not with water, it is possible to obtain the dihydrate of the ethyl ester of 4,4,4-trifluoro-2,3-dioxobutyric acid:[64]



As a result of the formation of trifluoroacetoxycarbonylcarbene on irradiation of α-diazotrifluoroacetoacetic ester and its homologue with ultraviolet light, it is possible to obtain from these substances heterocyclic compounds as a consequence of [2+3]-cycloaddition.[43,122–125] Thus the reaction with acetonitrile on irradiation affords oxazoles,[43,122,124,125] while the reaction with acetone produces a dioxolen.[123] The latter is hydrolysed by atmospheric moisture to the dihydrate of ethyl 4,4,4-trifluoro-2,3-dioxobutyrate:[123]



60—70%

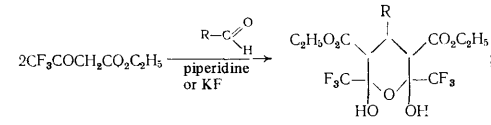


50%

$R_F = CF_3$, C_2F_5, C_3F_7.

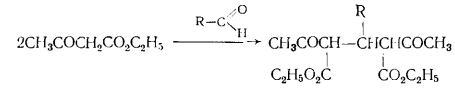
(c) Interaction with Aldehydes

TFAAE condenses with aldehydes, which involves the tetrahydropyran ring closure and the formation of 4-R-3,5-diethoxycarbonyl-2,6-dihydroxy-2,6-bis(trifluoroethyl)-tetrahydropyran:[126]

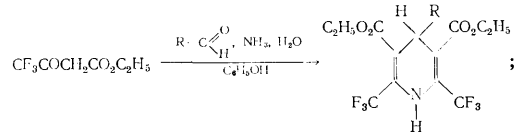


R = H (53%), CH_3 (55%), C_2H_5 (62%), C_6H_5 (19%), *p*-$CH_3C_6H_4$ (38%), *p*-FC_6H_4 (30%).

AAE reacts with aldehydes to form acyclic condensation products:[10]



In the Hantzsch reaction TFAAE apparently behaves in the same way as AAE,[10] forming 4-R-3,5-diethoxycarbonyl-2,6-bis(trifluoromethyl)-1,4-dihydropyridines:[127,128]



R = H, CH_3, C_2H_5, n-C_3H_7, C_6H_5, C_6H_4N, $O_2NC_6H_4$.

However, it has been stated that, in contrast to AAE, TFAAE involved in the Hantzsch synthesis gives rise to 2,6-dihydroxy-4-(*p*-nitrophenyl)-2,6-bis(trifluoromethyl)-piperidine-3,5-dicarboxylate, which does not split off water on treatment with sulphuric acid, acetic anhydride, titanium chloride, or dicyclohexylcarbodiimide.[129]

(d) Reactions of β-FKE Enolates

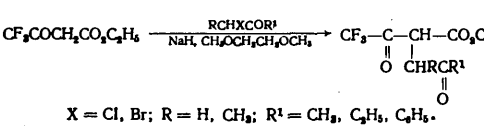
The β-KE enolate anions exhibit a dual reactivity, which depends significantly on the nature of the cation, the type of the ion pair, and the character of the solvent. These questions have been examined in detail in a review.[130] Here we shall deal only with data concerning β-FKE.

In order to account for the reactivity of the enolate anions derived from β-dicarbonyl compounds in alkylation reactions, a calculation based on the distribution of electron density in β-KE has been carried out by the LCAO-MO SCF method in the CNDO/2 approximation for the stable (*W*) and unstable (*U*) conformations of the enolate ions derived from malonic ester, AAE, TFAAE, and the chelate contact ion pair of the lithium enolate derived from AAE in the *U* conformation.[131] It has been shown that the highest negative charge is concentrated at the oxygen atom of the carbonyl group in all the enolate ions (in the *W* and *U* conformations). The introduction of the trifluoromethyl group (TFAAE) reduces the charge of the carbonyl oxygen and on the α-carbon atom of the enolate ion. A decrease of the basicity of the anion and of the alkylation rate constant corresponds to this effect.[132] It has also been established that the reactivity of the enolate ions and ion pairs derived from certain alkali metal enolates in alkylation reactions is controlled by the distribution of electron density in the highest occupied MO of the anion or its ion pair.[131] However, the negative charge on the carbonyl oxygen atom remains higher than on the α-carbon atom in all the structures; consequently the overall distribution of charges is

not the factor determining the result of the reaction, since the α-carbon atom is usually the preferred centre of attack. The distribution of electron density in the highest occupied MO of the anion or the ion pair derived from malonic and acetoacetic esters is consistent with the results of the alkylation, but the reactivity of the TFAAE anion is not controlled by the distribution of electron density in the highest occupied MO, since the alkylation reactions are in this case directed to the carbonyl oxygen atom. The presence of the trifluoromethyl group next to the carbonyl oxyen atom causes an additional increase of the negative electrostatic potential in the region of this atom compared with the region adjoining the α-carbon atom. The role of the electrostatic factor increases and the assumption that the alkylation reaction is controlled solely by electron density in the frontier MO becomes inadequate.[131]

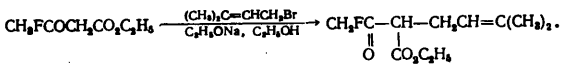
In the light of the above data, the experimental results obtained in the study of the kinetics and of the composition of the products of the alkylation of the sodium, potassium, and caesium enolates derived from AAE and its γ,γ-dimethyl and γ,γ,γ-trimethyl derivatives as well as TFAAE by ethyl tosylate in a highly aprotic solvent (hexamethylphosphoramide) become understandable.[132-134] The formation of only the *O*-isomer has been observed in the alkylation of the caesium enolate of TFAAE, while in the case of AAE and its fluorine-free derivatives, the products of both *O*- and *C*-alkylation are obtained. The effective rate constant for the ethylation of the caesium enolates decreases under these conditions in the sequence AAE > $(CH_3)_2CHCOCH_2CO_2C_2H_5$ > $(CH_3)_2CCOCH_2CO_2C_2H_5$ > TFAAE, while the acidity of β-KE diminishes in the opposite sequence. It has also been shown that, under the given conditions, the reacting species is only the enolate anion.[132,133]

The alkylation of TFAAE by α-chloro- or α-bromo-ketones in the presence of sodium hydride in dimethoxyethane gives rise to the *C*-alkylation products:[135-138]

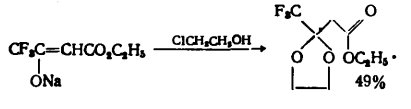


X = Cl, Br; R = H, CH_3; R^1 = CH_3, C_2H_5, C_6H_5.

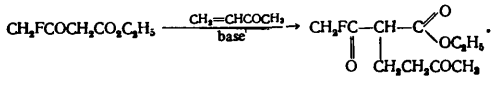
γ-Monofluoroacetoacetic ester is also alkylated at the carbon atom:[139]



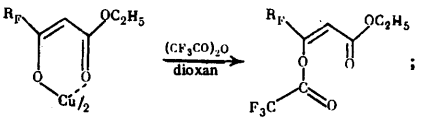
Interesting results have been obtained in the reaction of sodium enolate of TFAAE with ethylenechlorohydrin. This entails the formation of 2-ethoxycarbonylmethyl-2-trifluoromethyl-1,3-dioxolan,[140] while the sodium enolate of AAE reacts with ethylenechlorohydrin to form the *C*-alkylation product:[141]



In the Michael reaction with methyl vinyl ketone, γ-monofluoroacetoacetic and α,γ-difluoroacetoacetic esters give rise to the *C*-alkylation products:[142]

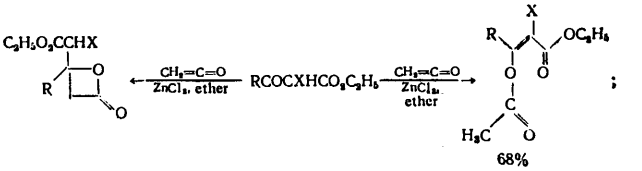


The copper chelates of β-FKE yield unstable *O*-acylation products on acylation with the anhydride of trifluoroacetic acid:[51]



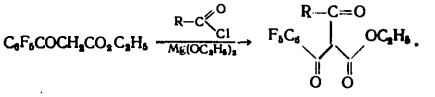
R_F = CH_2F, CHF_2, CF_3. 40-42%

It is of interest that γ-monofluoroacetoacetic ester and TFAAE react with keten to form *O*-acylation products, while α-monofluoroacetoacetic ester gives rise to the product of cycloaddition involving the keto-group under the same conditions, which the authors explain by the lower degree of enolisation of the α-fluoroester:[56]



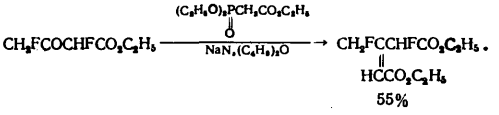
R = CH_3; X = F 68% R = CH_2F, CF_3; X = H.

The acylation of PFBAE by acid chlorides in the presence of magnesium ethoxide makes it possible to obtain *C*-acylation products, which is of interest for the synthesis of β-diketones with pentafluorophenyl groups:[119,143,144]



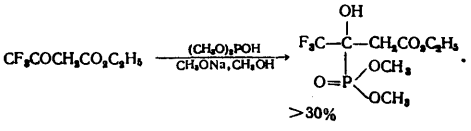
(a) Interaction with Phosphorus-containing Reagents

α,γ-Difluoroacetoacetic ester reacts with diethyl phosphonoacetate to form diethyl 4-fluoro-3-fluoromethylprop-1-ene-1,3-dicarboxylate:[17]



55%

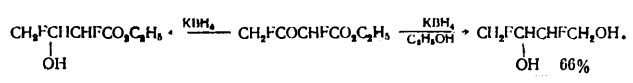
The reaction of TFAAE with dimethyl phosphite affords dimethyl 2-ethoxycarbonyl-1-hydroxy-1-trifluoromethylethylphosphonate:[56]



>30%

3. Oxidation-Reduction Reactions

The reduction of α,γ-difluoroacetoacetic ester with potassium tetrahydroborate involves only the carbonyl group or the ester and carbonyl groups depending on the reactant ratio:[13]



66%

Trifluoroacetoacetic ester reacts with sodium tetrahydroborate to give the product of the reaction of the carbonyl group while in the reaction with lithium tetrahydroaluminate both the carbonyl and ester groups are reduced:[145]

$$CF_3CHCH_2CO_2C_2H_5 \xleftarrow[\text{ether}]{NaBH_4} CF_3COCH_2CO_2C_2H_5 \xrightarrow[\text{ether}]{LiAlH_4} CF_3CHCH_2CH_2OH.$$
$$\quad OH \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad OH \quad 83\%$$

The reduction with hydrogen in the presence of Raney nickel, studied in relation to β-FKE with the heptafluoropropyl group, involves only the carbonyl group:[146–148]

$$C_3F_7COCH_2CO_2CO_3 \xrightarrow[Ni]{H_2} C_3F_7\underset{\displaystyle OH}{\underset{|}{C}}HCH_2CO_2CH_3.$$

The same reaction pathway obtains also in the biochemical reduction of β-FKE by bakers' yeast:[149]

$$R_FCOCH_2CO_2C_2H_5 \xrightarrow{\text{baker's yeast}} R_F\underset{\displaystyle OH}{\underset{|}{C}}HCH_2CO_2C_2H_5;$$
$$R_F = CF_3\,(92\%),\ C_7F_{15}\,(87\%).$$

Pentafluorobenzoylacetic ester is oxidised by selenium dioxide to ethyl pentafluorobenzoylglyoxylate:[82]

$$C_6F_5COCH_2CO_2C_2H_5 \xrightarrow[\text{toluene}]{SeO_2} C_6F_5C\overset{\displaystyle O}{\overset{\|}{-}}C\overset{\displaystyle O}{\overset{\|}{-}}C\overset{\displaystyle O}{\overset{\|}{-}}OC_2H_5.$$
$$(38\%)$$

V. APPLICATIONS

In most cases β-FKE are used as the starting materials for the synthesis of compounds with various useful properties. One of the aspects of the application of β-FKE is based on their capacity for complex formation with metal ions.[136,143,150–157] The β-FKE substituted in the α-position have been patented as extractants for the lanthanide and transuranic elements.[136,143] The chelate complexes of TFAAE with manganese, copper, cobalt, iron, and nickel have been recommended as antioxidants for various liquids and greases.[154] The copper and manganese chelates of β-FKE are effective catalysts in the formation of urethanes from isocyanates and alcohols.[155–157] β-Ketoesters with the heptafluoropropyl group are used as the starting materials for the synthesis of latexes used to impregnate fabrics in order to implant to them water-, oil-, and dirt-repelling properties and to reduce their susceptibility to inflammation.[146–148] TFAAE is used to obtain dyes suitable for the dyeing of synthetic fibres.[80]

The wide range of applications of derivatives of β-FKE such as coumarins,[114,116] pyridonaphthyridines,[112] and pyrroloquinolines [111] is based on their ability to fluoresce and to generate laser radiation.

7-Amino-4-trifluoromethylcoumarin and its salts with aminoacids and peptides are used as fluorescent markers for aminoacids and peptides in biological research.[114] Derivatives of 1,8-naphthyridine, 1,2-dihydropyrido[2,3-*b*]-1,8-naphthyridine, and 2*H*-pyrano[2,3-*b*]-1,8-naphthyridine exhibit a stable fluorescence in the range 393–482 nm in ethanol.[112] 1,6,6,7,8-Pentamethyl-2-oxo-4-trifluoromethyl-6,7-dihydro-1*H*, 2*H*, 8*H*-pyrido[3,2-*f*] indole serves as a source of blue laser radiation.[111]

Many derivatives of β-FKE exhibit physiological and pesticidal activities. α-Alkenyl derivatives of monofluoroacetoacetic ester have a hypocholesterolaemic activity.[86]

R-4-R^1-5-trifluoromethylfurans show coccidiostatic and growth accelerating activities.[135,138] Trifluoromethyltolylisoxazoles exhibit vasodilating, anticonvulsant, and muscle relaxing activities.[85] 1-Substituted 5-pyrazolones are diuretics.[81] 5-Trifluoromethylimidazoles behave as inhibitors of histamine activity.[92]

The ethyl ester of 2-acetoamido-4-trifluoromethylthiazolecarboxylic acid exhibits an antiinflammatory activity.[91] 6-(3-R-5-phenylisothiazolyl-4-formamido)penicillanic acids containing the trifluoromethyl group possess an antibacterial activity.[15]

The trifluoromethyl substituent is also present in thiazolino-5-pyrimidinones, which have been patented as analgesics.[98] Nicotinic and picolinic acids obtained from β-FKE exhibit analgesic and antipyretic activities.[105] 3,5-Diethoxycarbonyl-4-R-2,6-bis(trifluoromethyl)-1,4-dihydropyridines show cytotoxic, bacteriostatic, and hypotensive activities.[127,128] Derivatives of 3-trifluoromethylquinoline—analogues of quinine and quinidine—possess an antimalarial activity.[108–110] 5-Trifluoromethyl-2-R-quinolines are antiradiation reagents.[107] Benzothiopyrans containing fluorine exhibit an antimalarial activity.[118]

Fluorine-containing uracils possess herbicidal properties[69–71] and do not damage maize, flax, safflower, alfalfa, strawberries and gladioli.[88] 6-Trifluoromethyluracil has been used to synthesise 2-amino-6-trifluoromethylpurine, which is used as the antagonist of metabolites.[86] 4-Hydroxy-6-trifluoromethylpyrimidine is the starting material for the synthesis of insecticides.[89]

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Thus the introduction of fluorine atoms into the molecules of β-ketoesters is responsible for the appearance of a number of their characteristic features and leads to the alteration of the physicochemical properties, reactivities, and applied properties of these compounds and their derivatives. The existing data concerning their practical application make it possible to use fluorine-containing β-ketoesters and their derivatives in the national economy. At the same time, one should note the almost complete absence of studies of the reaction mechanisms and of the optimisation of the processes described, which undoubtedly holds back the further development of this field of organic chemistry.

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Halogenophilic Reactions Involving Derivatives of Four- and Five-coordinate Phosphorus

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The general aspects of halogenophilic reactions of phosphorus compounds have been examined. Examples of the reactions of the halides of four- and five-coordinate phosphorus with readily polarisable nucleophiles, taking place with the transfer of formally positive halogen, have been reviewed.
The bibliography contains 140 references.

CONTENTS

I. Introduction 1201
II. Reactions with organometallic compounds 1202
III. Reactions with three-coordinate phosphorus compounds 1204
IV. Reactions with alkenes and arenes 1205
V. Reactions with halide anions 1206
VI. Reactions with other readily polarisable nucleophiles 1207

I. INTRODUCTION

In the light of the general problem of nucleophilic reactions at a tetrahedral phosphorus atom, the transformations of its halides are of particular interest. The reason is that, because of their accessibility and high reactivity in nucleophilic reactions, phosphorus halides are the compounds on which the organic chemistry of this element is based.

The view is now generally held that in the reaction of phosphorus halides with nucleophilic reagents, the decisive step is the attack on the central atom, and the result is the formation of the products of halogen replacement.[1,2] At the same time there is a fairly large amount of experimental material on the reactions of the halides of four- and five-coordinate phosphorus with a number of nucleophilic reagents, leading to a decrease in the coordination number of the phosphorus atom. Their results cannot be interpreted in terms of replacement reactions. It is apparently for this reason that they have hardly ever been discussed in the theoretical examination of nucleophilic reactions with P^{IV} and P^{V} halides, and have not been reviewed before. In this respect, the situation that has arisen resembles that for nucleophilic reactions in organic halides. These processes have been studied in detail, and are generally interpreted in terms of replacement reactions at a carbon atom. It is found fairly frequently, however, that in spite of a high positive charge on the carbon atom, created by the negative inductive effect of the halogen atoms, for example in polyhalogenomethanes, nucleophilic attack at this atom is hindered. Usually, in these systems, it is directed to a peripheral atom, that is an S_{N^2Hal} reaction, or halogenophilic reaction, takes place, the result of which appears as the transfer of formally positive halogen.[3,4] The prerequisites for this reaction are shielding of the carbon atom by substituents and stability of the carbanion as the leaving group.[4] The ease of nucleophilic attack on the halogen increases in the order Cl ≪ Br < I,[5-8] and its probability increases with increase in the softeness and volume of the nucleophile.[6,9,10] It has been established that these reactions on the whole are characteristic of compounds in which the halogen atom is joined to a carbon atom carrying strong electron-acceptor substituents (ester, carbonyl, nitro-, and sulpho-groups).[5-9] Halogenophilic reactions are also assumed in the reactions of nucleophilic reagents with compounds containing N–Hal,[10-13] O–Hal, and S–Hal bonds.[10]

Comparison of the values of the constants σ_I, σ_m, and σ_n for phosphorus-containing substituents and for groups facilitating the manifestation by the halogen of the properties of an electropositive atom shows that the acceptor characteristics of the phosphorus fragments are similar to or even greater than the latter (see Table). This suggests that halogenophilic reactions should also be possible for compounds having a P–Hal bond. The halides of four-coordinate phosphorus should apparently show the greatest tendency to undergo these reactions. Unfortunately, the acceptor properties have not been determined quantitatively for halogenophosphonium cations, but spectroscopic studies of intramolecular interactions in four-coordinate phosphorus chlorides containing unsaturated groups have shown that the fragment PCl_3^+, for example, has a stronger action than the $POCl_2$ and $PSCl_2$ groups.[15-17]

Values of the constants σ_I, σ_m, and σ_n for different acceptor fragments.[14]

Group	σ_I	σ_m	σ_n	Group	σ_I	σ_m	σ_n
CCl_3	0.41	0.40	0.46	$PSCl_2$	0.59	0.70	0.80
COMe	0.23	0.36	0.47	PF_4	0.45	0.63	0.80
CN	0.57	0.56	0.66	$^+PMe_2PhI^-$	—	0.71	0.83
NO_2	0.68	—	—	$^+PPh_3Cl^-$	0.76	—	—
SO_2Ph	0.57	0.59	0.70	$^+PBu_3Cl^-$	0.60	—	—
PCl_2	0.45	0.53	0.61	$^+PMe_3I^-$	—	0.74	—
$POCl_2$	0.65	0.78	0.90	$^+PMePhI^-$	—	0.71	0.83

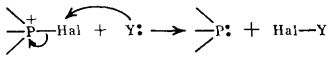
Useful information on the electron density distribution in the P–Cl bond in compounds of four-coordinate phosphorus can be obtained by ^{31}P NMR and ^{35}Cl NQR, which make it possible to characterise the electron environment of the two partners forming the bond.[18] Analysis of the relationship between the ^{35}Cl NQR frequencies and the ^{31}P NMR chemical shifts for R_nPOCl_{3-n}, R_nPSCl_{3-n}, and $R_nPCl_{4+n}^+$ showed that with increase in the electron-acceptor properties of the substituent in the compounds of each series,

the NQR frequency increases, and the NMR signal is displaced to a higher field. This is interpreted as a decrease in the polarity of the P–Cl bond. On going from phosphoryl to thiophosphoryl compounds and then to the chlorophosphonium analogues, the NQR frequency increases, and the shielding of the phosphorus nucleus decreases. Judging from the ^{35}Cl NQR spectra, the electron density on the chlorine atom decreases. Evidence in support of this explanation is provided by the recently measured asymmetry parameters of the electric field gradient at ^{35}Cl nuclei in chlorine-containing phosphorus compounds.[19] It was shown for the case of $POCl_3$, $PSCl_3$, and $PCl_4^+.AlCl_4^-$ that the asymmetry parameters of these four-coordinate phosphorus compounds are close to zero, possibly indicating that there is practically no interaction of the unshared electron pairs of the chlorine atom with the phosphorus atom.

A decrease in the polarity of the P–Cl bond may be indicated by the decrease in its length on going from phosphoryl and thiophosphoryl chlorides[20] to the tetrachlorophosphonium cation.[21]

Thus halogenophilic reactions among P^{IV} derivatives should be expected with the highest probability for halogenophosphonium compounds. The reactions of five-coordinate phosphorus halides involving the formation of these quasiphosphonium salts may take place similarly.

In these cases, in the reaction with soft bases,[22] the appearance of the products of the reduction of phosphorus to the three-coordinate state may be accompanied by the simultaneous oxidative chlorination of the nucleophile:



These reactions may not be heterolytic. A possible alternative is one-electron transfer processes. Their examination, however, is outside the scope of the present review, the aim of which was to summarise the reactions of four- and five-coordinate phosphorus halides, taking place with the transfer of formally positive halogen, which have not previously been systematised.

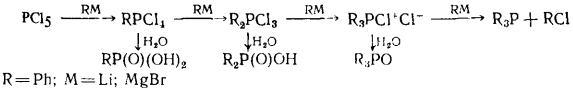
II. REACTIONS WITH ORGANOMETALLIC COMPOUNDS

A large number of reactions of phosphorus halides with organometallic compounds (OMC) are generally regarded as processes of nucleophilic substitution at the phosphorus atom.[23] At the same time, there are data indicating that a whole range of reactions of P^{IV} and P^{V} halides with OMC give products of the reduction of phosphorus to the three-coordinate state.

The first example of a reaction of this kind is the reaction of phosphorus pentachloride with phenylmagnesium bromide,[24] which gives triphenylphosphine in good yield. Reduction of PCl_5 is also observed in its reaction with *para*-trimethylsilylphenylmagnesium bromide.[25] The formation of the corresponding tertiary phosphine was detected in the reaction of phosphorus pentachloride with $PhC{\equiv}CMgBr$.[26]

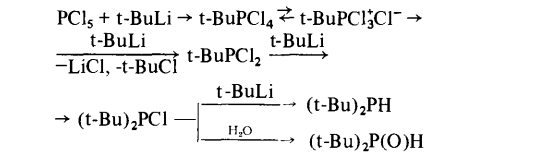
Comparatively recently, more thorough studies of these reactions were carried out, their synthetic possibilities were demonstrated, and a probable mechanism proposed. It was found that tertiary phosphines are obtained only by using an excess of OMC,[27,29,30] and that the yields of the reduction products increases with increase in the volume of the organic group in the OMC.[30] A detailed study of the products of the reaction of PCl_5 with an excess of phenyl-lithium showed that in addition to triphenylphosphine, an equivalent quantity of chlorobenzene is formed.[30] Decrease in the PCl_5 : PhLi ratio to 1 : 3 produces a fundamental change in the nature of the final product. Instead of the tertiary phosphine, its oxide is formed (after hydrolysis). Further decrease in this ratio leads to the formation of a mixture of the corresponding phosphonic and phosphinic acids.[31]

The results indicate that the reaction of five-coordinate phosphorus with phenyl derivatives of lithium and magnesium involve initially the successive replacement of halogen in the pentachloride molecule as far as the triorganodichlorophosphorane structure, whose ionised state makes possible a reduction process in subsequent reaction with the OMC:[31]



R = Ph; M = Li; MgBr

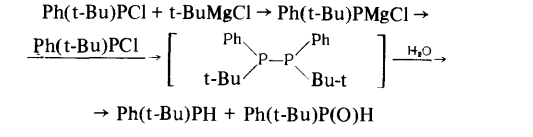
Increase in the volume of the group in the OMC molecule has a significant influence on the result of the reaction. The branching at the α-carbon atom in the isopropyl-lithium molecule leads to a marked increase in the yield of the reduction product.[29] The change to the t-butyl derivative leads to the formation of not the corresponding tertiary phosphine but a mixture of di-t-butylphosphine and di-t-butylphosphinous acid.[30] The presence of these products indicated that the reduction of five-coordinate phosphorus chloride takes place not at the triorganodichlorophosphorane stage but at an earlier stage, and is associated with the appearance of a chlorophosphonium intermediate:



The data obtained are consistent with the fact that it is impossible to replace directly all the chlorine atoms in the P^{III} compound by a t-butyl group, because of steric crowding at the phosphorus.[32,33] In this case the reaction of di-t-butylchlorophosphine, as reduction product, with an excess of the lithium alkyl gives a secondary phosphine, probably by a scheme including the transfer of a hydride ion from the lithium alkyl to the organophosphorus molecule.[32] Hydrolysis of the di-t-butylchlorophosphine remaining gives the secondary phosphine oxide (dialkylphosphonous acid).

Similar conclusions were reached in a study of the reaction of organic derivatives of phosphorus pentachloride with OMC.

The reactions of organyltetrachlorophosphoranes with an excess of an organolithium compound or Grignard reagent also give tertiary phosphines.[34–36] Increase in the volume of the group in the OMC increases the yield of reduction product.[36] The reaction of phenyltetrachlorophosphorane with t-butyl-lithium is influenced by steric and electronic factors. The expected di-t-butylphenylphosphine is not detected, and a mixture of t-butylphenylphosphine and its oxide appears.[30] The reaction probably takes place with the intermediate formation of t-butylphenylchlorophosphine, which subsequently reacts with the lithium alkyl to give the mixture of products indicated, by a scheme analogous to that proposed by Hoffmann for Grignard reagents:[33]



In this case the reduction of the five-coordinate structure at the phosphorus atom takes place at the t-butylphenyltrichlorophosphorane stage, which is different from the results

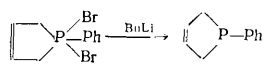
obtained in a detailed study of the reaction of phenyltetrachlorophosphorane with phenyl-lithium.[36] In the last case it was shown that the reduction and the formation of the equivalent quantity of chlorobenzene accompanying it take place at a reagent ratio of 1 : 3, that is at the stage of triphenyldichlorophosphorane formation.

In a study of the reaction of diphenyltrichlorophosphorane with phenyl-lithium in different proportions it was found that with equimolar quantities of the reagents, reduction of the phosphorane is not observed.[37] The hydrolysis of the reaction mixture gives triphenylphosphine oxide. The tertiary phosphine is formed only in a two-fold excess of the lithium aryl. The formation of chlorobenzene shows directly the halogenophilic character of the reaction. Reduction of Ph_2PCl_3 is also observed in the reaction with lithium alkyls. The yield of diphenylalkylphosphines increases with increase in the volume of the alkyl group in the organolithium compound.

The reactions of triorganotrihalogenophosphoranes with OMC have been studied in more detail. It was previously considered[38,39] that the reaction of triphenyldihalogenophosphoranes with alkylmagnesium halides gives triphenylalkylphosphonium salts. It was later established, however, that they are formed only with methylmagnesium iodide.[40] In other cases triphenylphosphine and the corresponding organic halide are obtained. Metallated derivatives of amines, pyrrole, and indole react with triphenyldihalogenophosphoranes to give aminotriphenylphosphonium salts.[41] The authors suggest that halogen transfer takes place at an intermediate stage:

$$Ph_3PHal_2 + RNHMgX \xrightarrow[-MgXHal]{} [Ph_3P + RNHHal] \rightarrow Ph_3P^+—NHR\ Hal^-$$

The reduction of cyclic dihalogenophosphoranes to the corresponding phospholenes under the influence of a lithium alkyl has been detected:[42]



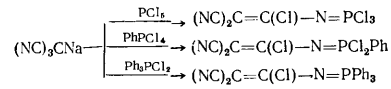
In a study of the reactions of organometallic compounds with chlorophosphoranes it was shown that the species responsible for the reduction of the phosphorus atom to the three-coordinate state are chlorophosphonium structures, either forming the basis of the chlorophosphorane structure or formed during the reaction.[27,36,37] To confirm this, the reactions were carried out between organolithium compounds and chlorophosphoranes shown by ^{31}P NMR,[43,44] ^{35}Cl NQR,[43–46] and ultraviolet spectroscopy[15–17] to be in the ionised state $R_nPCl_4^+{}_{-n}Cl^-$ in solution and in the solid state. For the reactions of $Ph_3PCl^+Cl^-$, $Ph_2EtPCl^+Cl^-$, *iso*-$Pr_3PCl^+Cl^-$, $Et_3PCl^+Cl^-$, *t*-$Bu_2PCl_2^+Cl^-$, and *iso*-$Pr_2PCl_2^+Cl^-$ it was shown that the presence of the chlorophosphonium cation in these compounds makes reduction possible under the influence of organic derivatives of lithium at the first stage of the reduction.[47] The organic halide is formed in quantities equivalent to the reaction product. The process was therefore interpreted in terms of halogenophilic attack on a chlorine atom in the phosphonium cation by the potential carbanion of the organometallic compound. Similar conclusions were reached in a study of the reactions of organolithium and organomagnesium compounds with organylchlorophosphonium hexachlorophosphates having a structurally fixed chlorophosphonium cation:[48,49]

$$R_nPCl_{4-n}^+\ PCl_6^- + R'Li \rightarrow R_nPR'_{3-n} + R'_3P + RCl + LiCl$$

R = Ph, p-ClC_6H_4, p-MeC_6H_4, p-$MeOC_6H_4$, PhCH=CH; R′ = Ph, Alk; n = 1–3

The absence of a chlorine atom in the phosphonium cation of the adduct $Ph_4P^+PCl_6^-$ makes its reduction by phenyllithium in the initial stages of the reaction impossible.[48]

Halogenophilic reactions apparently take place in the reaction of the sodium salt of tricyanomethane with phosphorus pentachloride and its organic derivatives:[50]



This is indicated by the formation of the same compounds by an independent method. Thus the expected products of the halogenophilic reaction of phosphorus pentachloride with $(NC)_3CNa$, namely PCl_3 and tricyanochloromethane, gave the same 1-trichlorophosphazo-1-chloro-2,2-dicyanoethylene.[50] An analogous reaction takes place between $(NC)_3CCl$ and triphenylphosphine.[51] Thus the first stage of the reaction of $(NC)_3CNa$ with P^V chlorides apparently involves halogen transfer:

$$R_nPCl_{5-n} + NaC(CN)_3 \rightarrow NaCl + [R_nPCl_{3-n} + ClC(CN)_3]$$

It is extremely probable that a similar process also takes place in the reaction of organyltetrachlorophosphoranes with malonodinitrile,[52] which is a strong CH acid (pK_a 11.0 [53]):

$$CH_2(CN)_2 + RPCl_4 \rightarrow HCl + [ClCH(CN)_2 + RPCl_2] \rightarrow NC—CH=C(Cl)—N=PCl_2R$$

Halogenophilic reactions can also be assumed in other cases with ionisation of CH acids:[54–56]

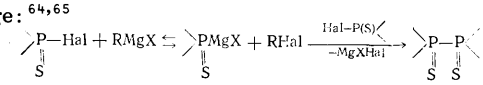
$$Ph_nPCl_{5-n} + CH_2X_2 \xrightarrow{Et_3N} Ph_nPCl_{3-n}=CX_2 + Et_3N\cdot HCl$$

X = COOEt, CN, SO_2Ph; n = 2, 3

The halogenophilic nature of the reaction is also indicated by result of the reaction of PCl_5 with a carbanion stabilised by resonance, such as phosphorus ylid:[57]

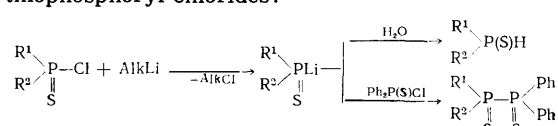
$$Ph_3P^+—\bar{C}(CH_2C_6H_4NO_2\text{-}n)COR + PCl_5 \rightarrow Ph_3P^+—C(Cl)\cdot(CH_2C_6H_4NO_2\text{-}n)COR$$

Among other reactions of OMC with P^{IV} derivatives, the transformations of the phosphoryl chlorides $R_nP(O)Cl_{3-n}$ have been most fully studied. They provide a familiar method for making a phosphorus–carbon bond, interpreted as nucleophilic replacement at the phosphorus atom.[23] The analogous reactions of thiophosphoryl chlorides have been less extensively studied. Work in this direction has established that phosphorus sulphide chlorides and arylthiophosphoryl dichlorides react with aryl-,[58] vinyl-,[59,60] and arylethynylmagnesium halides[60,61] to give tertiary phosphine sulphides. With lower alkylmagnesium halides, an "anomalous" Kabachnik reaction takes place[62,63] to give compounds with a phosphorus–phosphorus bond. The same products are formed with Grignard reagents and thiophosphoryl tribromide.[64] It has been suggested that the most probable scheme for this unusual reaction involves metal–halogen exchange:[64,65]



This scheme is confirmed by the formation of organic halides[49,65] and secondary phosphine sulphides (by hydrolysis of the exchange products).[66]

Organolithium compounds, which have an even greater tendency to undergo exchange reactions, react similarly with thiophosphoryl chlorides:[67]



R^1 = Cl, R^2 = Et, Ph, Cl; Alk = Et, Bu

This metal–halogen exchange reaction possibly takes place by a mechanism involving nucleophilic attack on the halogen. This model, for example, represents one probable scheme for the exchange reactions of organic halides.[68]

A curious feature is that increase in the concentration of the organolithium compound in the above reaction leads to the formation of tertiary phosphines.[69] This may be related to the reduction of the product of exchange by the lithium alkyl, the possibility of which was demonstrated by Trippett.[70]

Thus a soft base such as the potential carbanion of an OMC brings about reactions with various four- and five-coordinate phosphorus halides, whose results cannot be explained in terms of nucleophilic attack at phosphorus. A logical explanation of these reactions is provided by schemes including a halogenophilic reaction.

III. REACTIONS WITH COMPOUNDS OF THREE-COORDINATE PHOSPHORUS

Compounds of three-coordinate phosphorus are soft bases. It is evidently this property of P^{III} compounds that makes possible the unique reactions with polyhalogenohydrocarbons (Appel, Todd–Atherton, etc. reactions) and also with compounds containing an N–Hal or S–Hal bond. The large number of studies in this field have been summarised in several reviews,[10,71,72] where the preferred direction of these reactions, namely attack on the three-coordinate phosphorus compound at the halogen atom, is emphasised.

Similar reactions should naturally be expected for halides of four- and five-coordinate phosphorus.

Thus P^{III} compounds are fairly frequently used to reduce various halogenophosphonium derivatives.

For example, under the influence of phenyldichlorophosphine in the presence of phosphorus oxide chloride, methyldichlorophosphine is formed from the corresponding adduct of the Clay–Kinnear–Perren reaction:[73]

$$MePCl_3^+ AlCl_4^- + PhPCl_2 \xrightarrow{POCl_3} MePCl_2$$

The use of tributylphosphine instead of $PhPCl_2$ lowers slightly the yield of desired product. The reaction of $PCl_4^+SbCl_6^-$ with Bu_3P gives phosphorus trichloride and tributyldichlorophosphorane.[74] The reduction of the adducts $t\text{-}Bu_3PX^+MX_3^-$ (X = Cl, Br; M = Ge, Sn) by the action of $t\text{-}Bu_3P$ has been demonstrated;[75] the products are $t\text{-}Bu_3P.MX_2$ and $t\text{-}Bu_3PX^+X^-$. Another reaction between compounds of three-coordinate phosphorus and compounds containing a chlorophosphonium cation was discovered recently:[76]

$$Ph(R^1)PClX^+ AlCl_4^- + (R^2O)_2PR^3 \xrightarrow{H_2O} Ph(R^1)P(O)R^3$$

R^1 = Me, Et, s-Alk, CH_2OBu; R^2 = Et, Bu; R^3 = OR, OH, Cl; X = Cl, Br

It is suggested that the main stage of the reaction is halogen transfer:

$$\equiv P^+–Hal + (R^2O)_2PR^3 \rightarrow \equiv P: + HalP^+(OR^2)_2R^3$$

The reaction of the products of the Clay–Kinnear–Perren reaction with P^{III} compounds was recently studied in detail.[77] It was shown that these adducts can be reduced by triarylphosphines, triarylphosphites, and diethylaminodichlorophosphine. Chlorination of the reagent to give the corresponding chlorophosphonium salt takes place simultaneously:

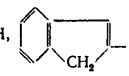
$$RPCl_3^+ AlCl_4^- + R'_nPCl_{3-n} \rightarrow RPCl_2 + R'_n PCl_{4-n}^+ AlCl_4^-$$

R = Cl, iso-Pr, CCl_3; R′ = Ph, PhO, *p*-MeOPhO (n = 3), Et_2N (n = 1)

Comparison of the results with data on the reaction of chlorophosphonium cations with nitrogen bases[78] shows that on going from hard compounds, for example pyridines, to soft compounds (P^{III} compounds) there is a fundamental change in the direction of attack by the base. Thus the phosphorus atom shows acceptor properties with respect to the unidentate pyridines, giving stable complexes $PCl_4^+.2Py$, whereas with three-coordinate phosphorus compounds the reaction centre is the chlorine atom, covalently bonded to phosphorus.

Salts of diethyl hydrogen phosphite exist predominantly in the form $(EtO)_2\overset{\cdot}{P}–O^-$ with three-coordinate phosphorus, and have been used to reduce various chlorophosphonium compounds.[79] The products of this reaction also correspond to the halogenophilic reaction scheme:

$$RPCl_3^+ PCl_6^- + 2(EtO)_2P\bar{O}\,H\overset{+}{N}Et_3 \rightarrow RPCl_2 + 2(EtO)_2P(O)Cl + PCl_3 + 2Et_3N\cdot HCl$$

R = PhCH=CH, PhOCH=CH, 

$RP(O)Cl_2$ and $(EtO)_2PCl$ are formed simultaneously in low yields, and this is attributed to the ambidentate character of the diethyl phosphite anion. In this case the oxygen atom, as a hard basic centre, attacks the phosphorus in the phosphonium cation:

$$RPCl_3^+ PCl_6^- + 2(EtO)_2P–O^- \rightarrow RP(O)Cl_2 + 2(EtO)_2PCl + 2Cl^- + POCl_3$$

The appearance of diethylchlorophosphite in the reaction mixture leads to the competing reaction involving the reduction of the original chlorophosphonium compounds under the influence of this tervalent phosphorus derivative:

$$RPCl_3^+ PCl_5^- + (EtO)_2PCl \rightarrow RPCl_2 + 2EtOP(O)Cl_2 + PCl_3 + 2EtCl$$

The presence of ethyl dichlorophosphate in the reaction products confirms that this reaction takes place.

This reaction of salts of diethyl hydrogen phosphite with chlorophosphonium derivatives is directly analogous to the familiar Todd–Atherton reaction, in which the main stage is halogen transfer:

$$CCl_4 + (RO_2)P–O^- \; H\overset{+}{N}R_3 \rightarrow CCl_3^-\overset{+}{H}NR_3 + (RO)_2\overset{Cl}{\overset{|}{P}}=O$$

It has been reported[80] that PH_3 reduces the products of the phosphorylation of alkenes by phosphorus pentachloride, which have a quasiphosphonium salt structure, to the corresponding dichlorophosphines in good yield. AsH_3 reacts analogously:[81]

$$3RPCl_3^+PCl_6^- + EH_3 \rightarrow 3RPCl_2 + 3PCl_3 + 6HCl + 2ECl_3$$

R = EtOCH=CH, BuOCH=CH, PhCH(Cl)–CH_2, BuCH(Cl)–CH_2; E = P, As

Methyldichlorophosphite is used fairly successfully to reduce unsaturated chlorophosphonium derivatives:[82,83]

$$\begin{matrix} R^1 \\ R^2 \end{matrix}\!\!>\!C=CHPCl_3^+ PCl_6^- \xrightarrow{CH_3OPCl_2} \begin{matrix} R^1 \\ R^2 \end{matrix}\!\!>\!C=CHPCl_2 + CH_3Cl + POCl_3$$

R^1 = Me, Et; R^2 = H, Me, Cl

Compounds of three-coordinate phosphorus are widely used to reduce phosphorus pentahalides and their organic derivatives.

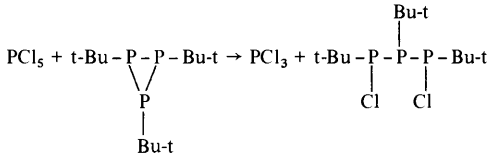
Conductometric[84] and ^{31}P NMR spectroscopic[74] studies of the reaction of phosphorus pentachloride with tertiary phosphines have shown that in the first stage of the reaction at a reagent ratio of 1 : 1, PCl_3 and the triorganyldichlorophosphorane are formed. The use of a two-fold excess of the pentachloride leads to the appearance of the triorganylchlorophosphonium hexachlorophosphate:

$$PCl_5 + R_3P \rightarrow PCl_3 + R_3PCl_2$$
$$R_3PCl_2 + PCl_5 \rightarrow R_3PCl^+ PCl_6^-$$

R = Ph, *p*-MeC_6H_4, *p*-$MeOC_6H_4$, *p*-$EtOC_6H_4$, Bu

The same result was obtained using phenyl- and diphenylchlorophosphines.[74]

Phosphorus pentachloride and pentabromide bring about the rupture of the phosphorus–phosphorus bond in tri-t-butylcyclotriphosphane:[85]

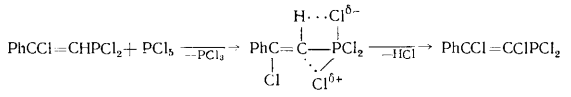


The chlorination of tri-*p*-cyclohexylphenyl phosphite to the corresponding dichlorophosphorane under the influence of phosphorus pentachloride takes place fairly readily.[86]

Unsaturated dichlorophosphines on treatment with PCl_5 give tetrachlorophosphoranes:[87,88]

$$PCl_5 + RCH{=}CHPCl_2 \rightarrow RCH{=}CHPCl_4 + PCl_3$$

The reaction of α-chlorostyryldichlorophosphine with the pentachloride, however, does not give a P^V derivative, because of the ease of the intramolecular chlorination at the vinyl carbon atom.



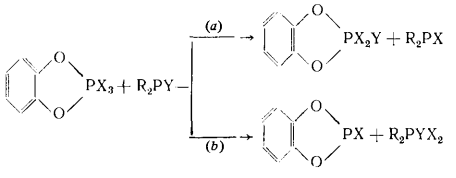
Methyl dichlorophosphite is used to reduce halogenophosphoranes:[89,90]

$$RPCl_4 + CH_3OPCl_2 \rightarrow RPCl_2 + CH_3Cl + POCl_3$$
$$R = Me,\ CCl_3,\ p\text{-}ClC_2H_4C_6H_4$$

Its use to convert distyryl- and tristyrylchlorophosphoranes into the three-coordinate state did not give satisfactory results. In this case, phosphoryl derivatives are obtained.[91]

The reduction of trihalogenophospholenes by triphenylphosphine, which is converted into the triphenyldihalogenophosphorane in the process, has been noted.[92]

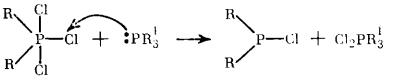
A series of studies of the reaction of P^V halides with compounds of three-coordinate phosphorus was carried out by Gloede and co-workers.[93–96] It was shown for the case of trihalogenodioxaphospholenes that cyclic halogenophosphoranes can undergo ligand exchange (*a*) and halogen transfer (*b*) with P^{III} derivatives:



R = Y = OEt, OPh; R = OPh, Y = Cl; X = Cl, Br

It is emphasised that the redox reactions (*b*) become preferred on going from the chlorides to the bromides of five-coordinate phosphorus.[94] This is consistent with the application of the principle of hard and soft acids and bases (HSAB) to halogenophilic reactions.

It has been suggested that the reduction of halides of five-coordinate phosphorus can take place not only with the participation of their halogenophosphonium form. Unionised trigonal bipyramidal halogenophosphoranes can also take part in halogenophilic reactions, and the reduction takes place as a result of attack on the halogen atom in the equatorial position by the soft base.[97] The electrophilic properties of this atom apparently arise as a result of the reaction of its unshared electron pairs with the phosphorus atom.[19] A similar intramolecular reaction has been assumed for other equatorial ligands.[98] This has been used to explain the reactions of various chlorophosphoranes with tertiary phosphines.[97] Phenyl- and diphenylchlorophosphoranes, which in weakly polar solvents have a trigonal bipyramidal structure with the organic substituents in the equatorial positions, are rapidly reduced by triphenyl- and tributylphosphines to the corresponding chlorophosphines. The reducing agent is converted into the triorganodichlorophosphorane:

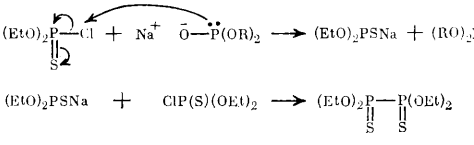


The reaction takes place analogously with CCl_3PCl_4 and $(CCl_3)_2PCl_3$, whose trichloromethyl substituents are in the apical positions.

Tertiary phosphines do not react, however, with triphenyldichlorophosphorane, which in non-polar solvents is probably present in the unionised form.[99] According to the apicophilicity rules,[100] the phosphorane in this form should have a trigonal bipyramidal structure with all the organic substituents in equatorial positions, which structurally excludes the appearance of Cl_{eq} and makes halogenophilic reactions impossible.

The successful use of white phosphorus to reduce P^{IV} and P^V halides can be explained in terms of halogenophilic reactions; the P_4 molecule can be regarded as a derivative of tervalent phosphorus. White phosphorus can reduce triorganodichloro-,[101] diorganotrichloro-,[102] and organotetrachlorophosphoranes,[103] trihalogenophospholenes,[104] and compounds containing a chlorophosphonium cation.[105–107]

Halogen transfer reactions under the influence of P^{III} derivatives are also observed in a number of thiophosphoryl halides. For example, unlike diethyl chlorophosphate, its thio-analogue reacts with sodium diethyl phosphite to give tetraethyl dithiohypophosphate:[108]



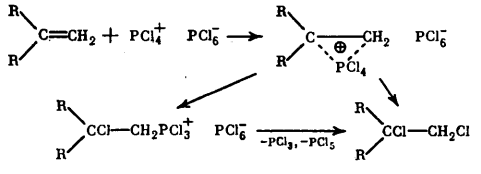
IV. REACTIONS WITH ALKENES AND ARENES

According to the HSAB principle, alkenes and arenes are regarded as soft bases, so that they can be expected to undergo reactions involving attack on a halogen atom in halogenophosphonium compounds or in derivatives of five-coordinate phosphorus.

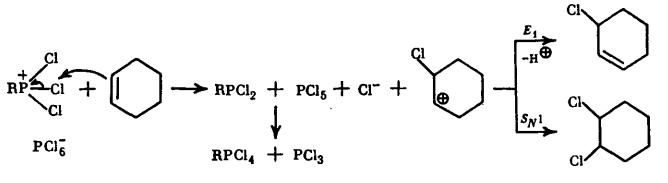
Thus phosphorus pentachloride and its organic derivatives have a chlorinating action on organic compounds of many classes, including various arenes.[109] In addition to the homolytic chlorination of alkylaromatic compounds in the side chain, a heterolytic reaction is also observed. This is indicated for example, by the chlorination of mesitylene to 2,4,6-trimethylchlorobenzene under conditions in which radical processes are inhibited.[110] An attempt was made to explain the chlorinating action of PCl_5 and its derivatives in terms of halogenophilic reactions at the chlorophosphonium cation, present in the crystalline pentachloride.[111] It was found that the model quasiphosphinium salts $PCl_4^+X^-$, where $X = AlCl_4$, BF_3Cl, $SbCl_6$, and PCl_6, and $Ph_nPCl_{4-n}^+PCl_6^-$ can, like PCl_5, chlorinate substituted benzenes in the ring. The ease of chlorination increases with increase in the electron-donor properties of the substituent in the arene. It was shown for the case of anisole that the formation of the chlorination product (*p*-chloranisole) is accompanied by the

simultaneous reduction of the phosphonium salt to three-coordinate phosphorus compounds. A necessary condition for the chlorination of the arene is the presence of chlorine in the phosphonium cation; thus the adduct $Ph_4P^+PCl_6^-$ cannot chlorinate anisole even under severe conditions.

Many authors[110,112,113] report a side reaction giving 1,2-dichloroalkanes in the phosphorylation of alkenes by phosphorus pentachloride. Moderate heating of the products of the phosphorylation of unsaturated compounds with an excess of an alkene in donor solvents (toluene, acetonitrile) also gives these dichlorides.[114] Increase in temperature and the polarity of the medium increases the chlorinating power of PCl_5 with respect to alkenes.[113] It is suggested that in polar media, phosphorus pentachloride ionises, and the resulting tetrachlorophosphonium cation reacts with the unsaturated compound.[110,113] The concerted opening of the epiphosphorane transition state leads to the production of a mixture of chlorination and phosphorylation products.



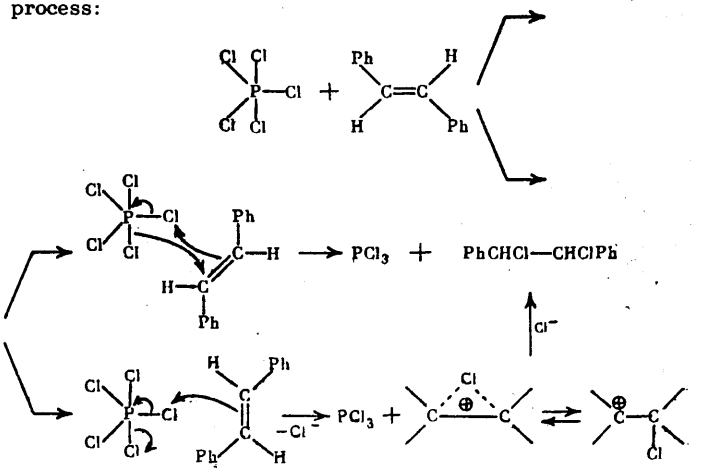
It has been shown for the case of the reactions of chlorophosphonium compounds with cyclohexene that the cation in $R_nPCl_{4-n}^+PCl_6^-$ (R = Ph, PhCH = CH; n = 1–3) is in fact responsible for the formation of alkene chlorination products.[115] Dephosphorylation of the original phosphorus-containing compound is not observed, however, and the corresponding chlorophosphoranes and phosphorus trichloride are formed. This fact, and also the presence of *trans*-dichlorocyclohexane and 3-chlorocyclohexene as alkene halogenation products provide evidence in support of a scheme involving halogenophilic attack by the alkene on the chlorine atom in the phosphonium cation:



Further evidence is provided by the increase in the difficulty of chlorinating cyclohexene with increase in the number of organic substituents in the cation, and by the fact that tetraphenylphosphonium hexachlorophosphate does not react.

It should be emphasised, however, that the formation of dichloroalkanes from alkenes and phosphorus pentachloride in weakly polar media (benzene, dichloroethane) as a result of the production of the halogenophosphonium cation in the reaction sphere does not agree with data on the state of PCl_5 in these solvents. Ultraviolet spectroscopy has shown convincingly that it is present in the unionised form.[116,117]

In a study of the chlorination of *trans*-stilbene by phosphorus pentachloride[118] it was suggested that this reaction be regarded as a halogenophilic reaction involving the unionised form of the phosphorus halide. The attack by the alkene takes place at the halogen atom in the equatorial plane of the trigonal bipyramidal PCl_5. The reaction can take place either as a concerted *anti*-addition or as a stepwise process:



V. REACTIONS WITH HALIDE ANIONS

From the above ideas about the preference of reactions with soft nucleophiles for achieving halogenophilic reactions, processes of this kind should be expected when halogenophosphonium compounds are treated with iodide and bromide anions:

$$\geq\overset{+}{P}\text{—Hal} + \text{Hal}'^- \rightleftarrows \geq P: + \text{Hal—Hal}'$$

The hard chloride anion should not be capable of bringing about these transformations.

Thus crystalline phosphorus pentachloride $PCl_4^+PCl_6^-$ is reduced to phosphorus trichloride by hydrogen iodide,[119] R_4NI,[120] and a mixture of KI and $R_4N^+Cl^-$.[121] PBr_5, which is also ionised in the solid state ($PBr_4^+Br^-$), reacts with tetraorganylammonium iodides to form PBr_3.[122] Analogous reactions take place with phosphorus pentaiodide.[123] All these transformations can be represented by the general scheme:

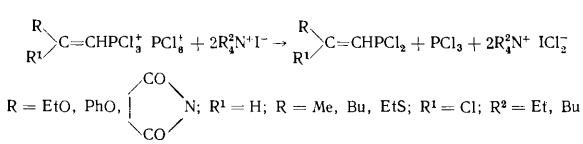
$$PX_5 + R_4N^+I^- \rightarrow PX_3 + IX + R_4N^+X^-$$
$$R_4N^+X^- + IX \rightarrow R_4N^+IX_2^-$$

In this case, tetraorganylhalogenoiodates are formed by the reaction of the interhalogen compound with the ammonium halide.

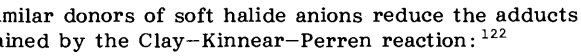
A similar scheme was observed for the reactions of phosphorus pentahalides with bromide anion donors.[120,122] As expected, the reaction of the chloride anion with chlorophosphonium compounds does not involve reduction. Derivatives of five-coordinate phosphorus are formed,[122,124] corresponding to attack by Cl^- on the phosphorus atom in the phosphonium cation.

It has been noted that the above equilibrium can be displaced towards the formation of reduction products not only by binding the interhalogen compound in a trihalide anion but also by complex formation with p-donors such as cyclic ethers and tertiary amines.[122] This makes it possible to carry out the reduction using potassium iodide.

The reduction of chlorophosphonium derivatives by tetraorganylammonium iodides has been extended to alkene phosphorylation products having a quasiphosphonium structure:[124]



Similar donors of soft halide anions reduce the adducts obtained by the Clay–Kinnear–Perren reaction:[122]

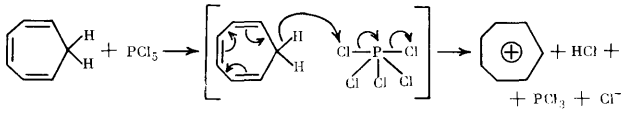


Here, however, it should be noted that if this reaction is carried out using alkyl iodides, spontaneous reduction of the products is observed;[125] this probably involves the I^- ion formed by the ionisation of the organic halide. The formation of triphenylmethylphosphonium salts by the action of methyl iodide on triphenyldihalogenophosphoranes[126] also involves halogen transfer.

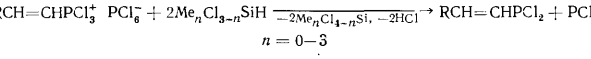
VI. REACTIONS WITH OTHER READILY POLARISABLE BASES

The hydride ion, as a soft base, should reduce phosphorus halides capable of halogenophilic reactions. This explains the reduction of triphenyldichlorophosphorane by lithium hydroaluminate[127] and of the adducts $RPCl_3^+AlCl_4^-$ by sodium and calcium hydrides.[128] The formation of tertiary phosphines in the hydrogenation of a large number of triorganodichlorophosphoranes by hydrogen in pyridine takes place for the same reason.[129]

The reaction of phosphorus pentachloride with cycloheptatriene to give tropylium chloride and phosphorus trichloride is explained by the transfer of a hydride ion to the halogen atom:[130,131]

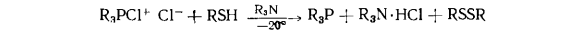


Silicon hydrides readily reduce the products of the phosphorylation of alkenes by phosphorus pentachloride:[132,133]



The reducing power of the silanes decreases with increase in the number of chlorine atoms in the molecule of the silicon-containing reagent. An analogous conclusion was reached in a study of the chlorination of silanes by phosphorus pentachloride.[134]

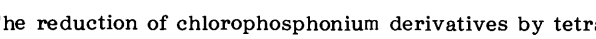
Sulphur-containing bases such as diorgano sulphides, thiols, the thiocyanate ion, and the thiosulphate ion are soft bases.[22] These reagents should also undergo halogenophilic reactions with phosphorus halides. Thus triphenyl- and tributyldichlorophosphoranes can be reduced by thiophenol and alkanethiols in the presence of triethylamine:[135]



Only small quantities of thiophosphoryl derivatives were formed. This last direction becomes preferred, however, in the reaction of chlorophosphonium derivatives with ethanethiol in the absence of a tertiary amine or with potassium thiocyanate.[136]

Sodium thiosulphate reacts with crystalline phosphorus pentachloride to give $POCl_3$, $PSCl_3$, and PCl_3 in the ratio 5 : 1 : 1. The formation of the last compound involves halogenophilic attack by the $S_2O_3^{2-}$ anion.[137]

The reduction of halogenophosphonium derivatives by carbon monoxide may be noted:[138]



Carbon monoxide is also chlorinated by triphenyldichlorophosphorane.[139] These data agree with the suggestion that the soft base carbon monoxide is capable of halogenophilic reactions.

Halogen transfer is also observed in the reaction of diphenyltrichlorophosphorane with tin(II) chloride.[140]

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The above experimental data show that halogen transfer processes are widely encountered in the chemistry of phosphorus halides. Although it is at present difficult to reach an unambiguous conclusion about the mechanism of these reactions, it can be seen that they are described fairly accurately by halogenophilic transformation schemes. In addition to the appearance of products of the reduction of the phosphorus halide, oxidative chlorination of the reagent is also generally observed. It can also be clearly seen that the decisive factor in these reactions is the softness of the base, and the application of the HSAB principle makes it possible to predict the final result fairly confidently.

The type of reaction examined above naturally should not be limited to the examples given, and the future appearance of new transformations which will extend even further the synthetic possibilities of halogen derivatives of phosphorus, an important preparative base in organophosphorus chemistry, can be expected.

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Isothiocyanates of Phosphorus Acids, *N*-Phosphorylated Thionocarbamates and Thioureas

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Current data on the synthesis, structures, the activities, and practical applications of the isothiocyanates of tri-coordinate, tetracoordinate, pentacoordinate, and hexacoordinate phosphorus acids and *N*-phosphorylated and *N*-thiophosphorylated thiocarbamates, dithiocarbamates, and thioureas are examined and surveyed.
The bibliography includes 223 references.

CONTENTS

I. Introduction 1210
II. Isothiocyanates of phosphorus acids 1210
III. *N*-Phosphorylated thiocarbamates and dithiocarbamates 1218
IV. *N*-Phosphorylated thioureas 1219

I. INTRODUCTION

Compounds in which the isothiocyanato-group is linked directly to the phosphorus atom have been attracting increasing attention by investigators, because, owing to their high reactivity, they serve as valuable starting materials and intermediates for the synthesis of a wide variety of organophosphorus compounds which are of both theoretical and practical importance.

Approximately 15 years have elapsed since the publication of the first reviews[1,2] devoted to the methods of synthesis, physicochemical properties, and applications of the isothiocyanates of phosphorus acids. During this period, the chemistry of phosphorylated isothiocyanates has developed further. It has now become necessary to survey and as far as possible arrange systematically the extensive and interesting data which have been published in recent years on this topic in the world chemical literature. Extremely unstable phosphorylated thiocyanates with the structure P–S–C≡N were synthesised and investigated for the first time during the last decade.[3-6] These compounds are intermediates in many methods of synthesis of isothiocyanates of phosphorus acids and for this reason we thought it desirable to consider them also in the present review.

According to patent data, the isothiocyanates of phosphorus acids have found applications as pesticidal[7,8] and bactericidal[9-12] preparations, as antitear and antiwear additives to lubricating oils,[13] as additives to natural and synthetic materials imparting fire resistance,[7,9,14,15] as stabilisers of polyoxymethylene,[16] as components of a cadmium-plating electrolyte which increase the corrosion resistance of the coating,[17] and as starting materials for the preparation of cation-exchange membranes.[18] In addition polymeric materials with fire-resistant properties whose molecules contain the P–N=C=S group have been synthesised.[19,20]

Among the products obtained from phosphorus-containing isothiocyanates, *N*-phosphorylated and *N*-thiophosphorylated thiocarbamates, dithiocarbamates, and thioureas occupy a special place in view of the wide variety of their practical applications. The methods of synthesis of *N*-(thio)phosphorylated thio- and dithio-carbamates, based on the reactions involving the addition of alcohols, alkoxides, mercapto-compounds, and certain acids to phosphorylated isothiocyanates, are therefore described in a special section of this review. The synthesis and properties of phosphorylated thioureas are examined in the concluding section of our review, which includes only data published after the review articles on phosphorus-containing thioureas.[1,21] In Sections III and IV we thought it essential to discuss not only the addition of various proton-donating reagents to the isothiocyanato-group but also other reactions leading to *N*-phosphorylated thio- and dithiocarbamates and thioureas. Heterocyclic derivatives in which the thiocarbamoyl group is incorporated in a ring are an exception; the chemistry of these compounds has been fairly completely described in another review[22] and is not considered in the present article.

II. ISOTHIOCYANATES OF PHOSPHORUS ACIDS

1. Methods of Synthesis

Various derivatives of tricoordinate, tetracoordinate, pentacoordinate, and hexacoordinate phosphorus containing the isothiocyanato-group linked directly to the phosphorus atom have now been obtained. Previous reviews[1,2] described the methods of their synthesis by the reactions of phosphorus acid halides with salts of thiocyanic acid or trimethylsilyl isothiocyanate, of partial esters of phosphorus(III) acids with thiocyanogen, of salts of dialkylphosphorodithioic acids with bromocyanogen, and of pyrophosphates and metaphosphonodithioates with potassium thiocyanate.

The first of the methods listed above continues to be the most convenient and most widely used because of the ready availability of the starting compounds.[3,4,7,23-40]

The interaction of phosphonochloridothioites with lead thiocyanate in ether leads to the formation of *S*-alkyl alkyl(aryl)phosphonoisothiocyanatidothioites (I):[23]

$$2R^1(R^2S)PCl + Pb(SCN)_2 \rightarrow 2R^1(R^2S)PNCS + PbCl_2. \quad (I)$$

The reactions of pentavalent phosphorus acids halides with potassium thiocyanate (or silver thiocyanate) yielded the corresponding isothiocyanates and dithiocyanates (II):[7,24-27]

$$R_nP(X)Hal_{(3-n)} + (3-n)\,KSCN \rightarrow R_nP(X)(NCS)_{3-n} + (3-n)\,KHal;$$
$$X = O, S;\ Hal = Cl, Br;\ n = 1, 2 \quad (II).$$

The reactions are usually carried out in acetone or acetonitrile between 5° and 100 °C.

Investigators have devoted much attention to the synthesis of isothiocyanates containing the phosphazene and other inorganic rings. Isothiocyanato-derivatives of phosphazenes (III) can be obtained by treating chlorophosphazenes with alkali metal or ammonium thiocyanates in organic solvents:[28]

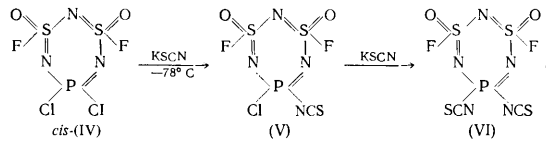
$$(NPCl_2)_n + 2n\text{KSCN} \rightarrow [NP(NCS)_2]_n + 2n\text{KCl};$$
$$n = 3, 4. \qquad \text{(III)}$$

The synthesis of fluoroisothiocyanatophosphazenes by the reaction of the corresponding monochloro- or monobromoperfluorophosphazenes with potassium or silver thiocyanate has been described.[29,30] Tetrachlorodiisothiocyanatocyclotriphosphazene has been synthesised by the reaction of $(NPCl_2)_3$ with potassium or ammonium thiocyanates.[31,32] Hexachlorodiisothiocyanato- and tetrachlorotetraisothiocyanatocyclotetraphosphazenes have been obtained analogously.[33]

It has been shown[34] that, on refluxing with KSCN in acetonitrile, 1,3,5-trichloro-1,3,5-triphenoxycyclotriphosphazene gives rise to a 96% yield of the corresponding triisothiocyanato-derivative. However, the reaction under the same conditions involving 1,3,5-tributoxy-1,3,5-trichlorocyclotriphosphazene yielded butyl thiocyanate and an oligometric product whose molecules were made up of phosphazene rings joined by P–O–P linkages and containing exocyclic butoxy- and thiocyanato-groups.

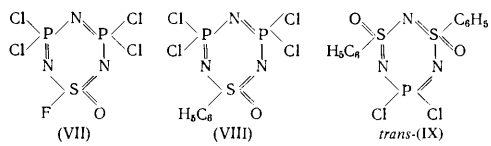
After treating compound (IV), having the *cis*-configuration, with potassium thiocyanate, the monoisothiocyanato-compounds (V) and the diisothiocyanato-compounds (VI) were isolated:[35]

Scheme 1



cis-(IV) (V) (VI)

Monoisothiocyanato-derivatives in the form of two (*cis*- and *trans*-) isomers have been obtained in proportions of 1:1 from compounds (VII) and (VIII) and compound (IX) having the *trans*-configuration:[36]



(VII) (VIII) *trans*-(IX)

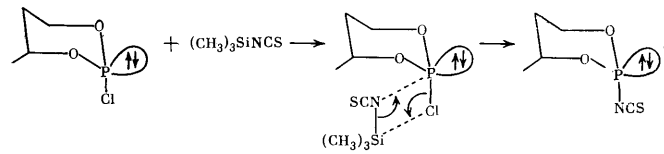
Two and four isothiocyanato-groups can be introduced into compounds (VII)–(IX) under appropriate conditions.[36]

The interaction of trimethylsilyl isothiocyanate with the chlorides of tricoordinate and tetracoordinate phosphorus acids may entail the complete exchange of halogen atoms for isothiocyanato-groups:[41,42]

$$R_{3-n}P(X)Cl_n + n(CH_3)_3SiNCS \rightarrow R_{3-n}P(X)(NCS)_n + n(CH_3)_3SiCl;$$
$$n = 1, 2, 3;\ X = \text{unshared electron pair of O and S.}$$

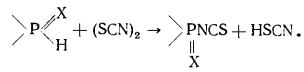
It has been demonstrated by ^1H NMR for the chloride of 1,3-butylenephosphorous acid that the reactions proceed stereospecifically with retention of the configuration at the phosphorus atom.[41] It can be shown that the reaction involves a cyclic electron transfer (Scheme 2), although one cannot rule out the possibility that the substitution takes place with the inversion and subsequent epimerisation of the reaction product at a high temperature:

Scheme 2



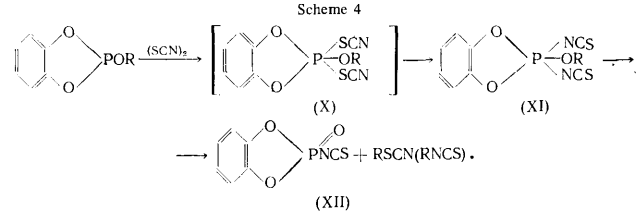
Various, including optically active, isothiocyanates of tetracoordinate phosphorus acids have been obtained in accordance with Scheme 3:[4,6,37]

Scheme 3



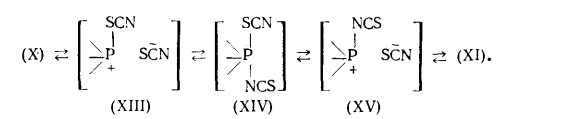
o-Phenylene phosphoroisothiocyanatidate (XII) is formed when alkyl *o*-phenylene phosphites are acted upon by thiocyanogen.[43] The diisothiocyanatophosphoranes (XI), which are stable at −40 °C and, for R = C_6H_5, also at room temperature, arise in the first stage of this reaction (Scheme 4). An increase of temperature leads to the decomposition of compounds (XI) into the phosphoroisothiocyanatidate (XII) and an alkyl thiocyanate or an alkyl isothiocyanate depending on the structure of the substituent R. When R was a primary alkyl group, an alkyl thiocyanate was formed but, when R was a secondary alkyl group, a mixture of thio- and isothio-cyanates was isolated:[44]

Scheme 4



(XII)

It has been suggested[43] that the reaction begins with the concerted addition of $(SCN)_2$ to the phosphorus atom with formation of the intermediate (X), whose conversion into the isomer (XI) is believed[43] to proceed via the equilibrium between the phosphonium structures (XIII) and (XV) and the phosphorane structure (XIV):



(XIII) (XIV) (XV)

The interaction of triphenylphosphine with thiocyanogen at −40 °C in CH_2Cl_2 leads to the phosphonium salt (XVI):[44,45]

$$(C_6H_5)_3P + (SCN)_2 \rightarrow (C_6H_5)_3\overset{+}{P}NCS\ \overline{SCN}.$$
$$\text{(XVI)}$$

When organophosphorus acids are added to the salt (XVI), phosphorylated isothiocyanates are formed in a high yield.[44] Phosphoranes and phosphonium salts of type (XI) and (XVI), containing isothiocyanato-groups, can also be obtained in a quantitative yield by the stepwise substitution of the chlorine atoms in the corresponding dichlorophosphoranes on treatment with trimethylsilyl isothiocyanates[46] or metal thiocyanates in the presence of a crown-ether.[44,46]

Phosphorus acid isothiocyanates are formed in the reactions of phosphorodithioic acids with cyanamides[47,48] and of phosphorothioic and phosphorodithioic acids with organic cyanates and thiocyanates[49–51] and also in the three-component reaction of diphenylphosphinous acid, ammonium

thiocyanate, and HCl.[52] None of these reactions are of preparative value for the synthesis of phosphorylated isothiocyanates because of the low yields and the difficulty of isolating pure products from the reaction mixture. However, a convenient method has been proposed for the synthesis of phosphoroisothiocyanatidothioates (XVII) [51,53] by the reaction of phosphorodithioic acids with an excess of alkyl thiocyanates at 80–100 °C:

$$R^1SCN + (R^2O)_2PSSH \xrightarrow{80-100^\circ C} \underset{(XVII)}{(R^2O)_2P(S)NCS} + R^1SH.$$

The reactions of bisphosphinyl disulphides (XVIII) with cyanide anion proceed via a stage involving the formation of the phosphinothioate anion (XIX) and the phosphinic thiocyanate (XX) which rearranges to the phosphinic isothiocyanate (XXI) (Scheme 5).[54] The final reaction products are the pyrophosphinomonothiomic anhydrides (XXII). When bulky substituents (for example, t-C_4H_9 or C_6H_5) are introduced at the phosphorus atom, the reactions stop at the stage involving the formation of the isothiocyanates (XXI):

Scheme 5

$$\underset{(XVIII)}{\left[R^1R^2P(O)S\right]_2} + CN^- \longrightarrow R^1R^2P(O)\!-\!S\!-\!S\!-\!P(O)R^1R^2 \longrightarrow$$
$$\longrightarrow \underset{(XIX)}{R^1R^2P(S)O^-} + \underset{(XX)}{\left[R^1R^2P(O)SCN\right]} \longrightarrow$$
$$\longrightarrow \underset{(XXI)}{R^1R^2P(O)NCS} + (XIX) \longrightarrow \underset{(XXII)}{R^1R^2P(O)OP(S)R^1R^2} + \bar{S}CN.$$

It has been shown by ^1H NMR that the fluoride of methylphosphonoisothiocyanatidic acid disproportionates with formation of the difluoride and the diisothiocyanate of methylphosphonic acid on heating (at 80 °C) for 10 weeks.[27]

In many cases phosphorylated isothiocyanates are synthesised by reactions of compounds already containing the P–NCS groups, which are accompanied by an increase of the coordination number of the phosphorus atom. Thus dialkyl phosphoroisothiocyanatidites enter into the Arbuzov reaction with alkylsulphenyl chlorides and are converted into *SO*-dialkyl phosphoroisothiocyanatidothioates (XXIV):[55]

$$\underset{(XXIII)}{(R^1O)_2PNCS} + R^2SCl \rightarrow \underset{(XXIV)}{(R^1O)(R^2S)P(O)NCS} + R^1Cl.$$

Vinyl phosphoroisothiocyanatidates and phosphorodiisothiocyanatidates can be obtained by means of the Perkow reactions from phosphoromono- and phosphorodiisothiocyanitidites, trichloroacetylphosphonate [40] and halogenopyruvate[56,57] esters, and hexachloroacetone.[57] Isothiocyanatospirophosphoranes have been synthesised by the reaction of the isothiocyanates of cyclic phosphorous acids with tetrachlorobenzoquinone [39] and dienes.[58]

A tetraisothiocyanato-derivative of hexacoordinate phosphorus (XXVI) has been synthesised from diaryloxytriisothiocyanatophosphorane (XXV) and tetraalkylammonium thiocyanate:[59]

$$\underset{(XXV)}{(C_6H_5O)_2P(NCS)_3} + Alk_4\overset{+}{N}\,N\bar{C}S \rightarrow \underset{(XXVI)}{(C_6H_5O)_2\bar{P}(NCS)_4}Alk_4\overset{+}{N}.$$

2. Phosphorothiocyanatidates and Their Rearrangement to Phosphoroisothiocyanatidates

In many of the reactions considered above one might have expected the initial formation of phosphorothiocyanatidates, which can rearrange to phosphoroisothiocyanatidates.

The first examples of phosphoroisothiocyanatidates were obtained as early as the beginning of this century, but were erroneously assumed to be the thiocyanato-derivatives.[1] The error was not corrected until the middle 1950's and in subsequent years it was established that phosphorothiocyanatidates are extremely unstable and exhibit a pronounced tendency towards isomerising to the isothiocyanatidates. The first reliable report of the synthesis of a phosphorothiocyanatidate, namely dineopentyl phosphorothiocyanatidate (XXVII), was published in 1972.[3] Compound (XXVII) was obtained by treating dineopentyl phosphorylsulphenyl chloride (XXVIII) with silver cyanide[3] or (better) with trimethylsilyl cyanide[60] in methylene chloride in the absence of atmospheric moisture and oxygen at −5 °C. At room temperature the rapid and irreversible rearrangement of the thiocyanato-derivative (XXVII) to the corresponding isothiocyanato-derivative (XXIX) is observed, the latter having being also synthesised by an independent procedure:

$$\underset{(XXVIII)}{[(CH_3)_3CCH_2O]_2P(O)SCl} + AgCN \rightarrow \underset{(XXVII)}{[(CH_3)_3CCH_2O]_2P(O)SCN}$$
$$\downarrow$$
$$[(CH_3)_3CCH_2O]_2P(O)Cl + KSCN \rightarrow \underset{(XXIX)}{[(CH_3)_3CCH_2O]_2P(O)NCS}.$$

Phosphorothiocyanatidothioates, which proved to be more stable than their oxygen analogues, have been synthesised by the same method.[4] Later new examples of the synthesis of similar compounds were published.[4–6,37,54,60–63] Stereochemical study of the rearrangement of phosphorothiocyanatidates to phosphoroisothiocyanatidates using diastereoisomeric cyclic[4,37] and optically active acyclic[5] model systems showed that it proceeds with total inversion of the configuration at the phosphorus atom. It has been noted that the isomerisation is accelerated in the presence of nucleophiles,[4,5] which was confirmed by the fact that carefully purified phosphorothiocyanatidates are stable in the absence of access by atmospheric oxygen. Their stability also increases in the presence of BF_3, which functions as a "nucleophile trapping agent".[4]

The authors suggest that the mechanism involving nucleophilic substitution at the phosphoryl centre is the most likely for the rearrangement.[4,5] Under the influence of atmospheric moisture or some other nucleophiles present in the reaction mixture at low concentrations, the thiocyanate anion is generated from the phosphorothiocyanatidates (XXX) via Scheme 6 at the beginning of the reaction. As a result of the nucleophilic attack by the nitrogen atom (a hard base) on the phosphorus atom of the thiocyanate anion (a hard acid centre) of the phosphorothiocyanatidate (XXX), the phosphoroisothiocyanatidate (XXXI) is then formed:

Scheme 6

$$Nu^- + \underset{(XXX)}{>P(X)SCN} \longrightarrow >P(X)Nu + S\bar{C}N;$$

$$S\bar{C}N + \underset{(XXX)}{X\!=\!P\!-\!SCN} \longrightarrow \left[\underset{(XXXII)}{SCN\!-\!\overset{X^-}{P}\!-\!SCN}\right]^{\neq} \longrightarrow$$

$$\longrightarrow \underset{(XXXI)}{SCN\!-\!P(X)<} + S\bar{C}N.$$

An addition–elimination mechanism with formation of a short-lived phosphorane intermediate having a trigonal-bipyramidal structure with the SCN groups in the apical positions cannot be ruled out, according to the authors,[5] for the substitution reaction considered. However, they give preference to the concerted mechanism with the transition state (XXXII) [reaction of the $S_N2(P)$ type] having the same geometry (Scheme 6).

Special investigations have shown[4,6] that many reactions leading to phosphoroisothiocyanatidates involve the formation of the corresponding thiocyanatidates as intermediates. The reactions of phosphorus acid halides with potassium thiocyanate have attracted particular attention in this connection. The available facts indicate that phosphorothiocyanatidates are not formed as intermediates in these reactions.

3. The Properties of Phosphoroisothiocyanatidates

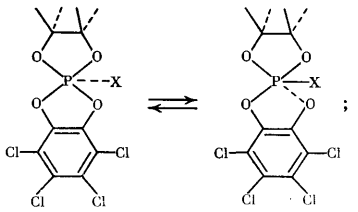
(a) Studies on Phosphoroisothiocyanatidates by Physicochemical Methods

Some data on the IR, NMR, and UV spectra of phosphorylatedisothiocyanates have been published in earlier reviews.[1,2]

In the IR spectra the ν_{as} absorption bands of the isothiocyanato-group linked to the phosphorus atom are in the range 1990–2000 cm^{-1};[29,64] in the range 730–910 cm^{-1}, intense ν(P–N) bands are present.[64] The ν(P=O) bands are located in the range 1220–1280 cm^{-1} [64] and the ν(P=S) frequencies are also close to the usual values.

It has been noted[35,36] that the introduction of the NCS group into the cyclic compounds (IV), (VII), (VIII), and (IX) induces an appreciable (up to 30 p.p.m. per NCS group) downfield shift of the signals due to the phosphorus nuclei in the ^{31}P NMR spectra.

By recording the NMR spectra over a range of temperatures, Trippett et al.[39] determined the free energy of activation ΔG^* for the pseudorotation (XXXIIIa) ⇌ (XXXb) of the isothiocyanato-group, which proved to be 17.8 kcal mol^{-1}.



(XXXIIIa) X = NCS, NCO, Cl (XXXIIIb).

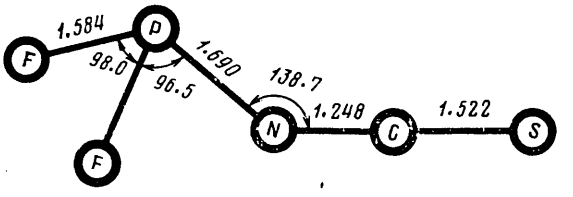
The quantity ΔG^* for the isocyanato-group is 17.5 kcal mol^{-1}. In terms of their apicophilic properties, both these groups (NCO and NCS) are close to the chlorine atom, for which ΔG^* is 17.8 kcal mol^{-1}.

The mass spectra of diethyl phosphoroisothiocyanatidate,[65] hexaisothiocyanatocyclotriphosphazene, and octaisothiocyanatocyclotetraphosphazene [66] have been investigated. The characteristic processes involving the decomposition of diethyl phosphoroisocyanatidate [65] involve the initial rupture of the P–N bond or the decomposition of ethoxy-groups, accompanied by the loss of the CH_3, C_2H_3, and C_2H_4 fragments. The mass spectra of cyclic isothiocyanates [66] indicate a greater stability of the phosphazene ring. The fragmentation of the NCS group takes place either with the elimination of the sulphur atom or with the loss of a S_2 molecule, or with the elimination of a CS_2 molecule. Data for the mass spectra of phosphoroisothiocyanatidates can also be found in other communications.[32,35,36,67]

The crystal and molecular structures of the isothiocyanates of trimeric [68] and tetrameric [69] cyclophosphazenes have been investigated by X-ray diffraction. The results have lead to the conclusion that the P–N linkage in the fragment

has a certain amount of double bond character.

A wider range of physicochemical methods have been used by investigators in the study of the molecular structure of difluoroisothiocyanatophosphine F_2PNCS (XXXIV).[70–73] The IR and Raman spectra in the gas phase, in the intermediate and far regions, have been obtained and discussed.[70,71] It has been demonstrated by photoelectron spectroscopy[72] that the lowest ionisation potentials in the molecule of compound (XXXIV) are those of the electrons of one of the π-bonds of the NCS group (10.2 eV) and the unshared electron pair of the phosphorus atom (11.9 eV). The parameters of the bond lengths and angles have been determined by electron diffraction[70] and have been refined[73] by employing a combination of electron diffaction and ^1H NMR methods in a liquid crystal solvent (see Figure). It has been shown[70] that the isothiocyanato-group is in the *trans*-position with respect to the FPF bisector.



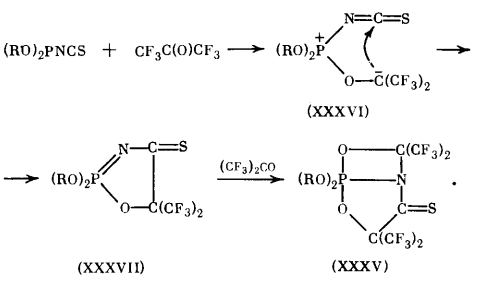
The bond lengths (Å) and valence angles (degrees) in the molecule of difluoroisothiocyanatophosphine (XXXIV).[173]

(b) Reactions of the Isothiocyanates of Phosphorus(III) Acids

Reactions involving an increase of the coordination number of the phosphorus atom and cycloaddition reactions with participation of the P̈N=C=S fragment, which plays the role of a 1,3-dipolar reagent, are most characteristic of phosphorus-(III) acid isothiocyanates.

The first example of the cycloaddition reaction has been described by Trippett and co-workers,[74] who investigated the interaction of hexafluoroacetone with dialkyl phosphoroisothiocyanatidites. A crystalline 1 : 2 adduct, the bicyclic phosphorane (XXXV), was obtained as a result:

Scheme 7



(XXXVI) (XXXVII) (XXXV)

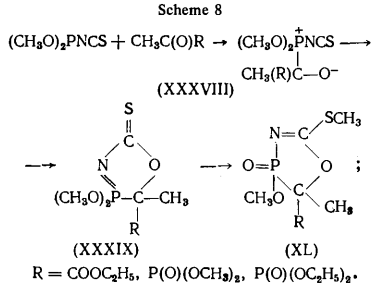
The betaine (XXXVI) (Scheme 7) is formed in the first stage and then cyclises to the imide (XXXVII), which is subjected to electrophilic attack by a second hexafluoroacetone molecule with the consequent formation of the bicyclic phosphorane

(XXXV). The strain in the trigonal bipyramid of the phosphorane becomes minimal, according to the authors,[74] when both rings occupy axial-equatorial positions and the nitrogen atom is then located in the equatorial position.

In subsequent studies a wide variety of carbonyl, imino-, and other unsaturated compounds were made to undergo the cycloaddition reaction with phosphorus(III) isothiocyanates.[40,75-78]

The interaction of dimethyl phosphoroisothiocyanatidite with acetyl phosphonates[75] and pyruvate esters[40] begins with nucleophilic attack by the phosphorus atom on the carbon atom of the carbonyl group. The dipolar ion (XXXVIII) cyclises to the intermediate (XXXIX) with a phosphimide linkage (Scheme 8). The subsequent imide–imide rearrangement with *S*-alkylation leads to substituted 3-methoxy-2-methyl-5-methylthio-3-oxo-1,4,3-oxaza-4-phospholens (XL):

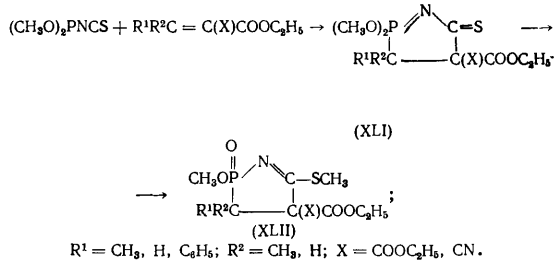
Scheme 8



(XXXVIII) (XXXIX) (XL)

R = $COOC_2H_5$, $P(O)(OCH_3)_2$, $P(O)(OC_2H_5)_2$.

In the reactions of dimethyl phosphoroisothiocyanatidite with esters of methylene- and ethylidene-malonic acids[76] and alkylidene derivatives of cyanoacetic ester,[77] the intermediates (XLI) with a P=N bond are also stabilised by the imide–imide rearrangement, being converted into *S*-alkylated products (XLII), which are formed as a mixture of the geometrical isomers:

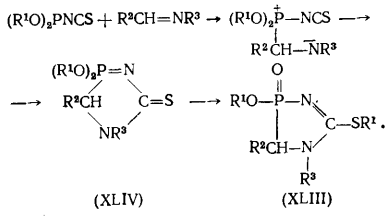


(XLI) (XLII)

$R^1 = CH_3$, H, C_6H_5; $R^2 = CH_3$, H; X = $COOC_2H_5$, CN.

It has been noted that the alkylidene derivatives of cyanoacetic ester are more reactive than the alkylidene derivatives of malonic ester as a consequence of the higher degree of polarisation of the double bond by the cyano-group.

The interaction of dialkyl phosphoroisothiocyanatidites with *N*-methylbenzylideneamine and *N*-phenyl and *N*-methyltrichloroethylideneamines results in the formation of 1,2-substituted 3-alkoxy-5-alkylthio-3-oxo-1,4,3-diaza-4-phospholens (XLIII):[78]

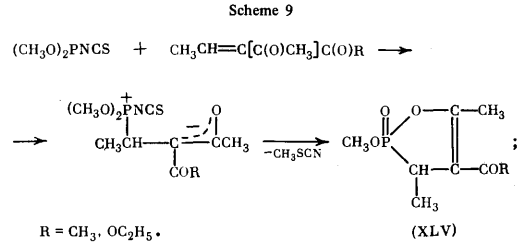


(XLIV) (XLIII)

When dimethyl phosphoroisothiocyanatidite was made to react with *N*-methyltrichloroethylideneamine, the authors isolated the products of the hydrolysis of the intermediate (XLIV) with a P=N bond—3-methoxy-1-methyl-3-oxo-2-trichloromethyl-1,4,3-diazaphospholan-5-thione.

In certain reactions of phosphoroisothiocyanatidites with unsaturated compounds the cycloaddition products involving the isothiocyanato-group are not formed and the pseudohalogen properties characteristic of this group are manifested. Thus the reactions of dimethyl phosphoroisothiocyanatidite with ethylideneacetylacetone and ethylideneacetoacetic ester lead to the formation of 4-substituted 2-methoxy-3,5-dimethyl-2-oxo-1,2-oxa-4-phospholens (XLV) and methyl thiocyanate (Scheme 9):[76]

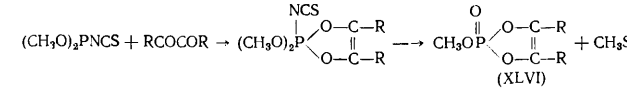
Scheme 9



R = CH_3, OC_2H_5. (XLV)

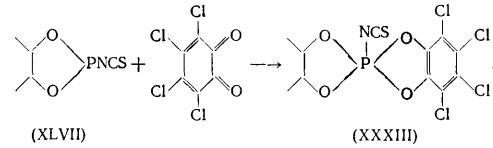
The reaction proceeds via a 1,4-cycloaddition mechanism with subsequent dealkylation in conformity with the second stage of the Arbuzov rearrangement.

The interactions of dimethyl phosphoroisothiocyanatidite with diacetyl and benzil lead similarly to the formation of 4,5-dimethyl- and 4,5-diphenyl-derivatives of 2-methoxy-2-oxo-1,3,2-dioxa-4-phospholens (XLVI):[79]



(XLVI)

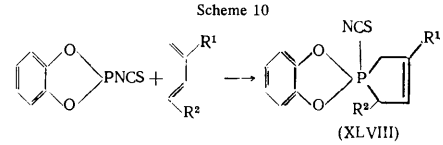
The reactions of α-dicarbonyl compounds with the isothiocyanates of cyclic phosphorous acids stop at the stage involving the formation of isothiocyanatospirophosphoranes, which is illustrated by the formation of compound (XXXIII) by the reaction of isothiocyanates of the 1,3,2-dioxaphospholan series (XLVII) with tetrachloro-*o*-benzoquinone:[39]



(XLVII) (XXXIII)

An analogous reaction in accordance with Scheme 10, which results in the formation of isothiocyanatophosphoranes (XLVII), takes place when *o*-phenylene phosphoroisothiocyanatidite reacts with 1,3-dienes, such as divinyl, isoprene, piperylene, and chloroprene:[58]

Scheme 10

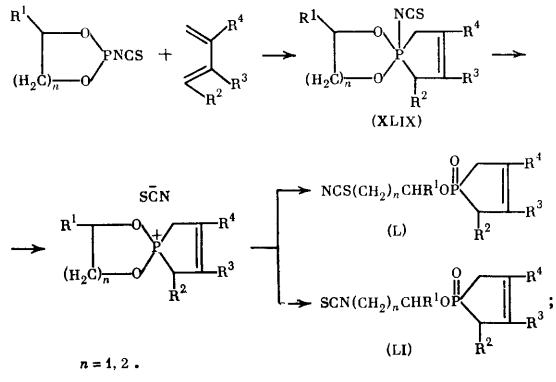


(XLVIII)

The reactivity of the dienes in condensation with phosphoroisothiocyanatidites decreases in the sequence isoprene > divinyl > piperylene > chloroprene. These data permit the conclusion that the phosphorus-containing component behaves as an electrophile. The condensation of ethylene and 1,3-butylene phosphoroisothiocyanatidites[80,81] with the same dienes does not stop at the isothiocyanatophosphorane (XLIX) stage. The phosphorane undergoes the second stage of the

Arbuzov rearrangement, giving rise to compounds of tetracoordinate phosphorus (L) and (LI):

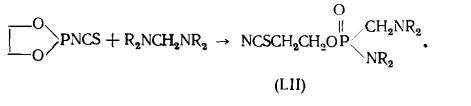
Scheme 11



The reactions with piperlyene and 2,3-dimethylbuta-1,3-diene afford only the thiocyanates (L), while in the case of divinyl, isoprene, and chloroprene two products were isolated in each case: the thiocyanate (L) and the isothiocyanate (LI).

After the thiocyanate anion has been removed from the intermediate adduct (XLIX) (Scheme 11), it can attack the most hydrogenated carbon atom of the ester group via the sulphur or nitrogen atom. Attack via the sulphur atom is preferred, because the highest negative charge is concentrated on it at the instant of the removal of the thiocyanate anion. Indeed in all cases the yield of thiocyanates predominates.

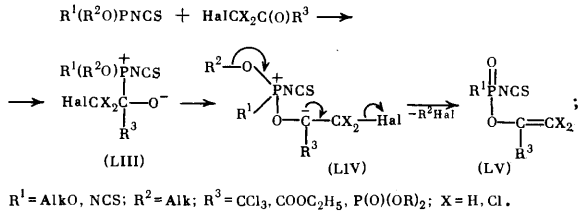
Treatment of ethylene phosphoroisothiocyanatidite with various methylenediamines including dipiperidinylmethane and di-4-morpholinylmethane yielded thiocyanatoethyl aminomethylphosphonamidates (LII).[82] These reactions apparently proceed via a mechanism similar to that described above:



(LII)

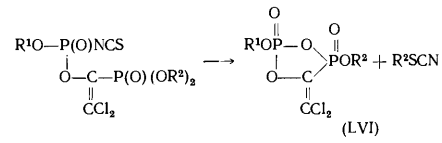
Phosphoromono- and phosphorodi-isothiocyanatidites react with α-halogenocarbonyl compounds to form the products of the Perkow reaction via Scheme 12. This has been demonstrated in relation to halogenopyruvate esters,[56,57] hexachloroacetone,[57] and trichloroacetylphosphonate esters.[40] In these reactions phosphoroisothiocyanatidites behave like trialkyl phosphites. According to Scheme 12, the reactions begin with the nucleophilic attack by the phosphorus atom on the carbon atom involved in the C=O bond with formation of the dipolar ion (LIII), which undergoes the phosphonate–phosphate rearrangement to the dipolar ion (LIV). The subsequent elimination of the alkyl halide leads to the vinyl phosphates (LV).

Scheme 12



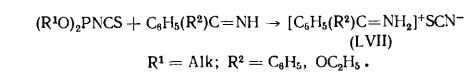
R^1 = AlkO, NCS; R^2 = Alk; R^3 = CCl_3, $COOC_2H_5$, $P(O)(OR)_2$; X = H, Cl.

The vinyl phosphates, formed in the reaction with trichloroacetyl phosphonates, are capable of cyclising to a dioxadiphospholans (LVI):[40]



(LVI)

The main product of the reaction of dialkyl phosphoroisothiocyanatidites with imines having a mobile hydrogen atom, for example, with diphenylketimine and benzimidoethyl ether, are immonium thiocyanates (LVII). The structure of the phosphorus-containing products was not established:[78]



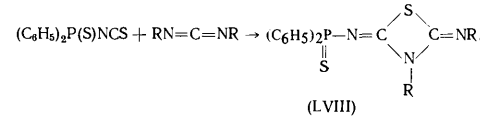
(LVII)

R^1 = Alk; R^2 = C_6H_5, OC_2H_5.

(c) Reactions of the Isothiocyanates of Tetracoordinate Phosphorus Acids

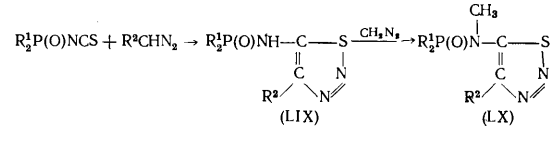
Reactions involving the addition of various nucleophiles to the NCS group are most characteristic of the isothiocyanates of tetracoordinate phosphorus acids. These reactions will be considered in the corresponding Sections devoted to the methods of synthesis of N-phosphorylated thio- and dithiocarbonates and thioureas. In the present Section we shall deal with other reactions of the isothiocyanates of tetracoordinate phosphorus acids, mainly their cycloaddition reactions.

The reactions of diphenylphosphinothioic isothiocyanate with dicyclohexyl- and diisopropyl-carbodiimides, leading to 1,3-thiazetidine derivatives (LVIII), and not 1,3-diazetidine derivatives as had been stated previously in the literature, have been described:[83]



(LVIII)

The interaction of phosphorylated isothiocyanates with diazomethane or phenyldiazomethane leads to the formation of the corresponding 5-(*N*-phosphinyl)amino-1,2,3-thiadiazoles (LIX):[84]

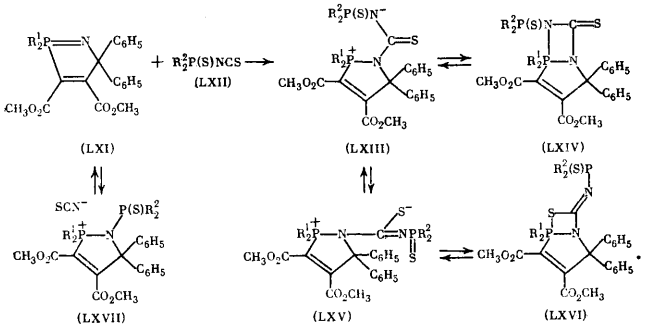


(LIX) (LX)

When the reactions are carried out with a large excess of diazomethane, 5-(*N*-methyl-N-phosphinyl)amino-1,2,3-thiadiazoles (LX, $R^2 = CH_3$) are formed. The involvement of phenylphosphonic diisothiocyanate and phosphoric triisothiocyanate in these reactions does not lead to the expected thiadiazoles, but the structure of the products formed has not been established. Dimethyl- and diphenyl-phosphinothioic isothiocyanates react with azaphospholans (LXI) to form cyclic [2 + 2]-adducts.[85] The phosphorylated isothiocyanates (LXII) (as well as isothiocyanates without phosphorus) add via the C=S bond to the phosphazine group in azaphospholes (LXI) with formation of compounds (LXVI)

containing the 1,3,2-λ^5-thiazaphosphetidine ring:

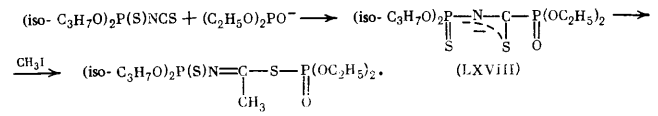
Scheme 13



When compounds (LXVI) are dissolved, the equilibrium (LXVI) ⇌ (LXV) ⇌ (LXIII) ⇌ (LXIV) is established. In the case of the dimethylphosphinyl group, it is displaced towards the form (LXIV) to a greater extent than in the case of the diphenylphosphinothioyl group. With increase of temperature to 70–90 °C, the reversible migration proceeds so rapidly that the ^{1}H NMR spectra exhibit a coalescence of the δ_{PCH_3} signals for (LXIV) and (LXV). The rearrangement proceeds intramolecularly and not via the reverse dissociation (LXVI) ⇌ (LXI) + (LXII) ⇌ (LXIV), which is demonstrated by the fact that the azaphosphole (LXI) added in excess is not involved in the coalescence. Yet another isomer-adduct (LXVII) is formed when the reaction is carried out in benzene, from which it crystallises.

It has been established by ^{31}P NMR that compound (LXVII) is converted into an equilibrium mixture of compounds (LXIV) and (LXVI) via compounds (LXIII) and (LXV) in $CHCl_3$ and more slowly in a benzene suspension.

The mesomeric anion (LXVIII) formed in the reaction of diisopropyl phosphoroisothiocyanatidothioate with sodium diethyl phosphite exhibits the 1,2-C → S mitration of the phosphoryl group in methylation:[86]



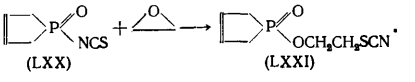
The SCN group manifests pseudohalogen properties in certain reactions of the isothiocyanates of tetracoordinate phosphorus acids. For example, phosphorylated aminoheterocycles of type (LXIX) are formed (Scheme 14) in the reactions with aminobenzazoles, benzazolone imines,[87] 2-aminothiazoles, and 2-aminothiazolines:[88]

Scheme 14

$$R^1R^2P(X)NCS + H_2NHet \rightarrow R^1R^2P(X)NHHet + HNCS;$$
(LXIX)

Het = heterocyclic group

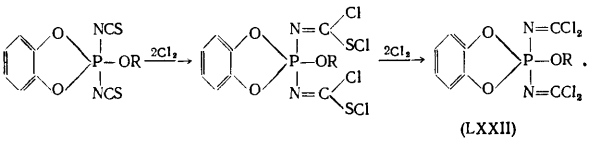
Epoxyethane is capable of being inserted in the P–N bond of the phosphorylated isothiocyanates. Isothiacyanatophosphine oxide (LXX) has been converted in this way into the 2-thiocyanatoethyl phosphinate (LXXI):[80]



The reaction with molecular chlorine, leading to phosphorylated isocyanide dichlorides (see, for example, Roessky and Janssen[30] and Derkach and Liptuga[89]), are extremely characteristic of the isothiocyanates of phosphorus acids. Many other examples of similar reactions have been quoted in a review.[1]

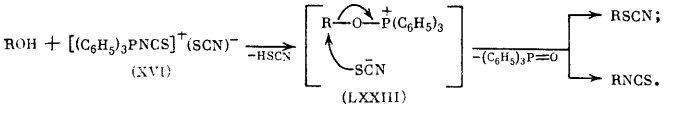
(d) Chemical Reactions of Isothiocyanates with the Phosphorane or Phosphonium Structure

Alkoxydiisothiocyanato-*o*-phenylenedioxyphosphoranes are smoothly chlorinated at −80 °C by 4 moles of chlorine to give compound (LXXII):[43]



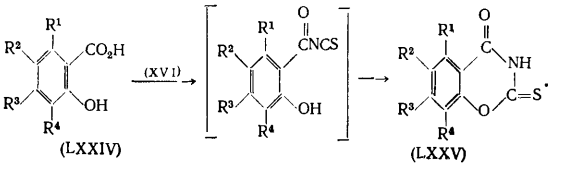
The adduct of triphenylphosphine and thiocyanogen—the phosphonium salt (XVI), described in 1977,[45] permits the synthesis of thio- and isothio-cyanates, disubstituted thioureas, amides, phosphimides, and other compounds in high yields and under mild conditions.[44,45,90–98] The adduct converts via Scheme 15 primary alcohols into thiocyanates, tertiary alcohols into isothiocyanates, and secondary alcohols into a mixture of both products[44,45] in almost quantitative yields:

Scheme 15



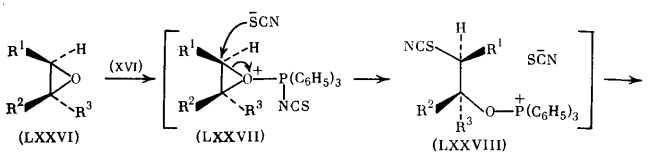
The reactions proceed via the intermediate (LXXIII), the formation of thio- or isothio-cyanates depending on the ambident character of the thiocyanate anion. Carboxylic acids give rise to acyl isothiocyanates in this reaction.[44]

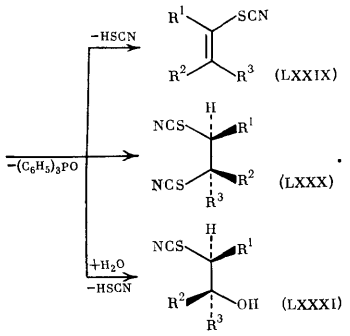
2-Thiono-3,4-dihydro-2*H*-1,3-benzoxazin-4-ones (LXXV) have been obtained in 70% yields by treating substituted salicylic acids (LXXIV) with the salt (XVI):[90]



The epoxides (LXXVI) react with the phosphonium salt (XVI) via Scheme 16 under mild conditions with the opening of the oxiran ring and the formation of mono- and di-isothiocyanato-derivatives.[94,98] The interaction of α,β-epoxyketones leads to α-thiocyanatovinyl ketones (LXXIX, R^1 = R^4CO). Regiospecific thiocyanation of monosubstituted or 1,2-disubstituted epoxides leads to the corresponding vicinal dithiocyanates (LXXX), *threo*-dithiocyanates and *erythro*-dithiocyanates being formed respectively from *trans*- and *cis*-epoxides. The reactions of 1,1-disubstituted epoxides give rise to vicinal *threo*-thiocyanatohydrins (LXXXI):

Scheme 16

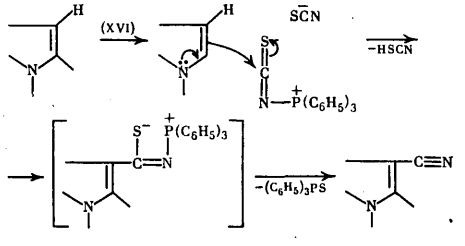




It has been suggested[98] that the electrophilic phosphorus atom of the phosphonium salt (XVI) attacks the oxygen atom of the oxiran ring with formation of the intermediate (LXXVII), which is then subjected to nucleophilic attack by the thiocyanate anion. This results in the opening of the oxiran ring and the formation of the β-thiocyanatoalkoxyphosphonium salt (LXXVIII), resembling the intermediate formed in the reactions with alcohols. In the case of α,β-epoxyketones the intermediate (LXXVIII) undergoes ready α-deprotonation by the thiocyanate anion, accompanied by the spontaneous elimination of triphenylphosphine oxide and the formation of α-thiocyanatovinyl ketones (LXXIX). The regiospecificity of the reactions can be accounted for by the stabilising effect of the neighbouring carbonyl group.

The intermediate (LXXVII), formed from monosubstituted and 1,2-disubstituted epoxides, is attacked by the thiocyanate anion at the least substituted carbon atom. A second SCN group then displaces triphenylphosphine oxide from compound (LXXVIII) via nucleophilic substitution with formation of vicinal dithiocyanates (LXXX). When the substitution by the thiocyanate anion is hindered by steric factors, as happens, for example, in the intermediate (LXXVIII) obtained from 1,1-disubstituted epoxides, hydrolysis takes place readily and leads to the formation of vicinal thiocyanatohydrins (LXXXI) and triphenylphosphine oxides.

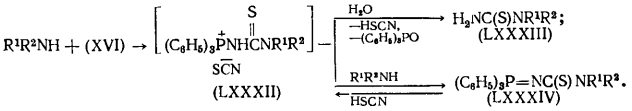
The use of the phosphonium salt (XVI) makes it possible to achieve the cyanation of pyrroles, indoles, and enamines under mild conditions and in satisfactory yields.[45,97]



The cyanation of pyrroles takes place selectively in the 2-position when the latter is unsubstituted. Otherwise, the cyano-group is introduced into the less reactive 3-position. The reactions of the salt (XVI) with indoles also proceed selectively with formation of products in which the cyano-group is in the 3-position. If an alcoholic group is present in the indole or pyrrole molecule, then its thiocyanation takes place in competition with the cyanation of the heterocycle. However, the introduction of an acyl protecting group makes it possible to avoid the first reaction.

Yet another application of the phosphonium salt (XVI) involves its use in the synthesis of substituted thioureas and amides.[91-93,95] In the first stage of the reactions with the amines, the phosphonium salts (LXXXII) are formed (Scheme 17), being converted into the corresponding 1,1-disubstituted thioureas (LXXXIII) in a high yield on treatment with aqueous acetonitrile:[91,95]

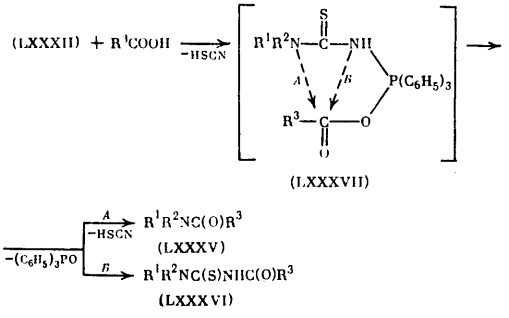
Scheme 17



The intermediate formation of compound (LXXXII) has been confirmed by chemical reactions. When the phosphonium salt (XVI) is treated with an excess of the amine, the phosphine imine (LXXXIV) is formed and is smoothly converted into the corresponding thiourea and triphenylphosphine oxide when it is treated with an aqueous solution of thiocyanic acid.

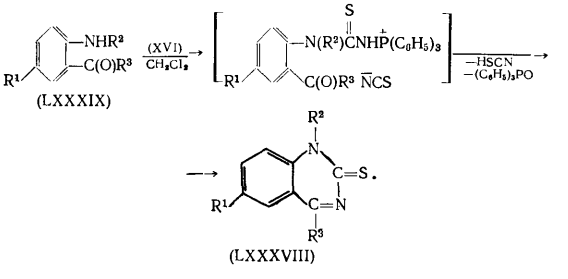
If carboxylic acids are introduced into the reaction instead of the aqueous acetonitrile, the corresponding amides (LXXXV) and/or acylthioureas (LXXXVI) are formed, depending on the structure of the initial amine and carboxylic acid:

Scheme 18



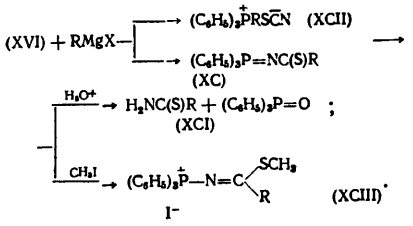
The reactions apparently begin with the attack by the carboxylate anion on the phosphorus atom in the salt (LXXXII) and lead to the intermediate (LXXXVII). The latter split off triphenylphosphine oxide and are converted either into the amide (LXXXV) via a six-membered cyclic transition state (pathway *A*) or into the acylthiourea (LXXXVI) via a four-centre transition state (pathway *B*). With the increase of the size of the substituents in the amine and the carboxylic acid, the yield of the amides (LXXXVI) diminishes, while that of the thioureas (LXXXVI) increases, which can be accounted for by the smaller dependence of the reaction via pathway *B* on the steric factor, because in this case the substituents can be located in the *trans*-position.

The adduct of triphenylphosphine with thiocyanogen (XVI) has been used also in the synthesis of 2-thiono-1,2-dihydroquinazolines (LXXXVIII) from readily available *o*-acylanilines (LXXXIX):[92,95]



The reaction of organomagnesium compounds with the adduct (XVI) proceeds with formation of phosphine imine intermediates (XC) which are converted into the thioamides

(XCI) on acid hydrolysis:[93]



In the absence of acid, it is possible to isolate compound (XC) and a small amount of the phosphonium salt (XCII). The phosphine imine (SC) is methylated by methyl iodide to the phosphonium salt (XCIII).

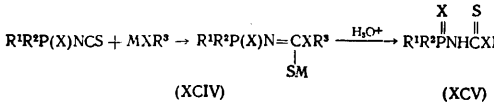
Thus the reaction of alcohols, epoxides, carboxylic acids, and organophosphorus acids and the adduct of triphenylphosphine and thiocyanogen begins with the nucleophilic attack on the phosphorus atom, which leads to the formation of phosphonium salts of the type (LXXIII) and (LXXVII). The reactions with amines, enamines, organomagnesium compounds, pyrroles, and indoles begin with the nucleophilic addition to the NCS group. Depending on the structure, the intermediates formed in these reactions on treatment with different reagents give rise to a whole range of practically important substances.[93]

III. *N*-PHOSPHORYLATED THIO- AND DITHIOCARBAMATES

It is known that the esters of tetracoordinate phosphorus acids and derivatives of thio- and dithio-carbamic acids constitute the two most numerous classes of chemical substances among the pesticidal preparations employed nowadays. The study of the biological activity of phosphorylated thio- and dithio-carbamates, in the molecule of which phosphorus-containing and thiocarbamate fragments are combined, is therefore of great interest. Substances with bactericidal,[11] antihelminthic,[99-101] insectoacaricidal,[102-105] and other pesticidal activities[106-108] have been found among *N*-phosphorylated thio- and dithiocarbamates. In addition, *N*-phosphorylated thiocarbamates can be used as antioxidants for synthetic resins and as additives to motor fuels,[104] while *N*-thiophosphoryldithiocarbamates can be employed as complex-forming agents and extractants.[109]

1. Methods of Synthesis of *N*-Phosphorylated Thio- and Dithio-Carbamates

The synthesis of organophosphorus thio- and dithiocarbamates from phosphorus-containing isothiocyanates or mixtures of tetracoordinate phosphorus acid chlorides and potassium thiocyanate on treatment with alcohols, mercaptans, or, better, with their metal derivatives has been described.[1] The *S*-metallated derivatives of *N*-(thio)phosphorylated isothio(dithio)carbamates (XCIV) formed in the latter case are converted into thio(dithio)carbamates (XCV) after acidification:

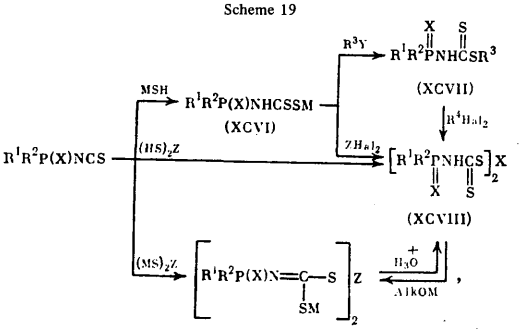


where X = O or S and M is an alkali metal. These metals have remained of key importance also in subsequent studies. Thus *S*-butyl-*N*-diphenylphosphinyl dithiocarbamate has been obtained by the reaction of diphenylphosphinyl isothiocyanate with sodium butanethiolate in the presence of triethylamine on subsequent treatment with NH_4Cl.[110]

The addition of alcohols to the NCS groups of 1,1,3,3-tetrachloro-5,5-diisothiocyanatocyclotriphosphazene,[31,32] 3,9-diisothiocyanato-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5,5]undecane 3,6-dioxide, and the analogous bissulphide [104] led to the formation of the corresponding phosphorus-containing bisthionocarbamates.

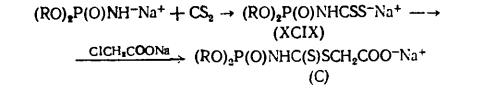
The salts of *N*-(thio)phosphorylated dithiocarbamic acids (XCVI), formed when the thioisocyanates of tetracoordinate phosphorus acids are treated with alkali metal hydrogen sulphides,[105,106,111-116] are converted into the dithiocarbamates (XCVII) on alkylation.[103,106,113] Reaction of the salts (XCVI) with alkylene or oxydimethylene dihalides leads to bisphosphoryldithiocarbamates (XCVIII):[105,117]

Scheme 19

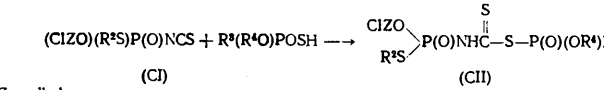


where X = O or S, M = Li, Na, K, or NH_4, Y = halogen or Ts [tosyl? (Ed.of Translation)], and Z = $(CH_2)_2O$ or a substituted or unsubstituted alkylene. In addition, compounds (XCVIII) can be obtained by treating phosphoroisothio(thio)cyanatidates with dithiols[99,117-119] or alkali metal dithiolates with subsequent acidification[101-103,105,117] and also by the reaction of dithiocarbamates (XCVII) with alkylene dihalides in the presence of bases.[117]

The possibility of obtaining *S*-sodium dialkylphosphoryldithiocarbamates (XCIX) from sodium phosphoramides and carbon disulphide has been demonstrated.[120] When compounds (XCIX) are treated with sodium chloroacetate, the paste-like sodium *S*-[*N*-(dialkylphosphoryl)thiocarbamoyl] acetates (C) are formed:

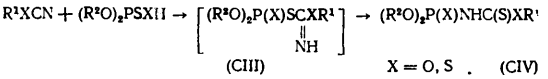


Certain acids can also be made to add to the isothiocyanato-group. In particular, the partial esters of phosphonomonothioic acids interact with phosphoroisothiocyanatidothioates (CI) to form *NS*-diphosphorylated dithiocarbamates (CII):[108]



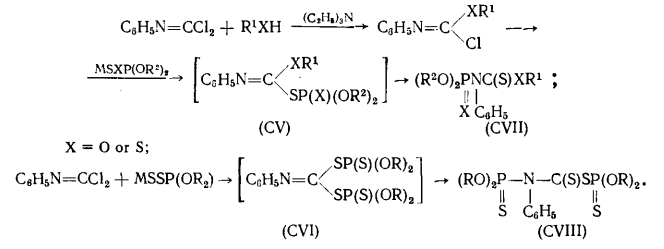
Z = alkylene.

Phosphoromonothioic and phosphorodithioic acids are capable of adding tothe C≡N bond in cyanates and thiocyanates, the adducts (CIII) rearranging readily to *N*-(thio)phosphorylated thio- or dithio-carbamates (CIV):[50,51]

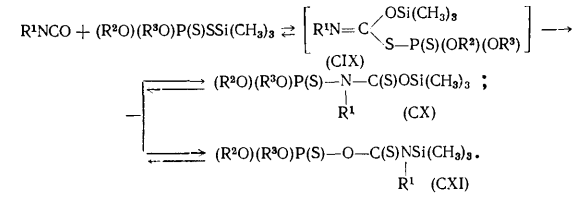


When the chlorine atoms in phenyl isocyanide dichloride are substituted via a series of stages by an alkoxy- or alkylthio-group and then by a dialkyl phosphorothioate or phosphorodithioate group (Scheme 20), *S*-(thio)phosphorylated isothio- or isodithio-carbamates (CV) are formed.[107,121] The interaction of phenyl isocyanide dichloride with salts of dialkylphosphorodithioic acids lead to analogous compounds (CVI).[107,122] However, in contrast to patent data,[123–125] it has been shown[107,121,122] that compounds (CV) and (CVI) are unstable and in the course of the process undergo an irreversible rearrangement to the phosphorylated dithiocarbamates (CVII) and (CVIII). When salts of dialkylphosphoromonothioic acids are involved in the reaction, derivatives with a P=O group are produced:[107,121]

Scheme 20

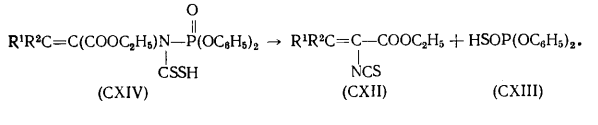


The interaction of *S*-trimethylsilyl phosphorodithioates with isocyanate leads to the adducts (CIX) which are capable of reversible isomerisation to both *N*-thiophosphorylated [compounds (CX)] and *O*-thiophosphorylated [compounds (CXI)] trimethylsilyl thionocarbamates:[126]

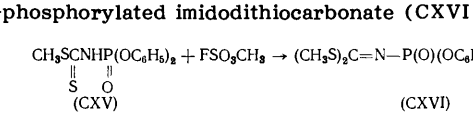


2. The Properties of *N*-Phosphorylthiocarbamates

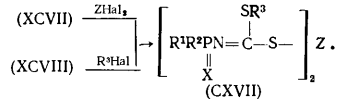
The reactions involving the addition of alcohols and mercaptans to the isothiocyanates of tetracoordinate phosphorus acids are reversible.[1] Even at room temperature *N*-(thio)phosphorylated thio- and dithio-carbamates (CIV) decompose to phosphoroisothio(thio)cyanatidates and alcohols or thiols.[50,51] An interesting decomposition into the isothiocyanate (CXII) and diphenylphosphoromonothioic acid has been observed on heating dithiocarbamates having the structure (CXIV):[127]



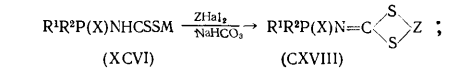
In the study of the concentration and temperature dependence of the IR spectra of solutions of *S*-alkyl *NN*-dialkylthiophosphoryldithiocarbamates, no thione–thiol tautomerism has been observed.[109] Nevertheless the alkylation of *N*-(thio)phosphorylated thio- and dithio-carbamates by different alkylating agents always leads to *S*-alkylated and not *N*-alkylated products. Thus, on treatment with methyl fluorosulphate, the dithiocarbamate (CXV) is converted into the *N*-phosphorylated imidodithiocarbonate (CXVI):[128]



Diphosphorylated bisimidodithiocarbonates (CXVII) are formed on reaction of *N*-phosphorylated dithiocarbamates (XCVII) with alkylene dihalides[103] and of diphosphorylated dithiocarbamates (CXVIII) [99,102,117,119] or their metal derivatives[103,118] with alkyl halides:

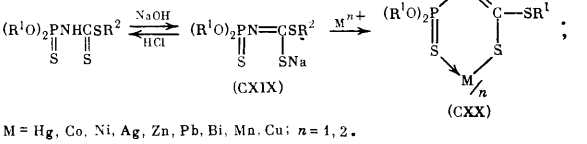


On treatment with alkylene dihalides in the presence of bases, the salts of *N*-(thio)phosphoryldithiocarbamic acids (XCVI) cyclise to *N*-(thio)phosphorylated imino-1,3-dithietans[106,111,112,115,116,129–136] or imino-1,3-dithiolans (CXVIII),[114] which have found practical application as broad spectrum pesticides:



Z = alkylene.

N-Thiophosphorylated dithiocarbamates are weak acids with $pK_a \cong 7.5$ (in aqueous alcoholic mixtures) [51,109] and are converted on treatment with alkalies into water-soluble *S*-metal derivatives (CXIX):[51]



M = Hg, Co, Ni, Ag, Zn, Pb, Bi, Mn, Cu; $n = 1, 2$.

Treatment of derivatives of compound (CXIX) by salts of thiophilic metals leads to the formation of stable complexes (CXX), which can be extracted from organic media by organic solvents, which makes it possible to employ *S*-alkyl-*NN*-dialkylthiophosphoryldithiocarbamates as extractants.[109]

IV. *N*-PHOSPHORYLATED THIOUREAS

Numerous publications devoted to the methods of synthesis and reactions of *N*-phosphorylated thioureas and also to their practical use in industry, agriculture, medicine, and veterinary science have appeared in recent years.

Numerous investigations have been devoted to the biological activity of *N*-phosphorylated thioureas. According to literature data, substances exhibiting carcinostatic and immunostimulating,[137] bactericidal,[10–12,138–142] anthelminthic,[55,143–154] arthropocidal,[55,155] nematocidal,[55,143,155,156] insectoacaricidal,[104,143,156,157] herbicidal,[140,157,158] fungicidal,[38,157,159–163] and other pesticidal[107,164,165] activities as well as preparations used to destroy ectoparasites,[166] for the prophylaxis and treatment of coccidiosis,[167] and in the therapy of radiation sickness[168] have been found among them.

In addition, the use of *N*-phosphorylated thioureas as additives to lubricating oils[169,170] and motor fuels,[104,171,172] as antioxidants for synthetic resins,[104] as additives to reduce the combustibility of organic substances,[14,15,171–174] as fire-resistant polymeric materials,[19,20] as plasticisers,[165] and as extractants[175,176] is of extremely great value.

1. Methods of Synthesis of *N*-Phosphorylated Thioureas

The method of synthesis of *N*-phosphorylated thioureas most frequently employed involves the addition of ammonia,[37,104] aliphatic amines,[5,6,30–32,51,54,60,67,104,110,143,148,155,156,164,168,169,177–179] aromatic amines,[38,47,49–51,104,110,141,146–149,151,152,154,159–162,164,169,177,178,180–186] and heterocyclic amines[38,104,137–139,141,142,159,163,164,169,186] to the NCS group in the isothiocyanates of tetracoordinate phosphorus acids. Reactions with alkylene-diamines[144,157,169] and arylenediamines[145,147,149,150,166,187,188] result in the formation of bisphosphorylated thioureas. The corresponding *N*-phosphorylated thiosemicarbazides have been isolated in the reactions with hydrazines.[38,138,139,189–191] The reactions usually proceed very readily at room temperature and lead to the formation of the required compounds in high yields.

The kinetics of the reactions of phosphoroisothiocyanatidates with aniline have been studied by IR spectroscopy:[180]

$$R_2P(O)NCS + C_6H_5NH_2 \rightarrow R_2P(O)NHC(S)NHC_6H_5\ ;$$
$$R = C_2H_5,\ C_6H_5O,\ C_2H_5,\ C_2H_5O.$$

It was found that the reactions are of second kinetic order. Phosphorylated isothiocyanates and phenyl isothiocyanates can be arranged in the following sequence in terms of their reactivities:

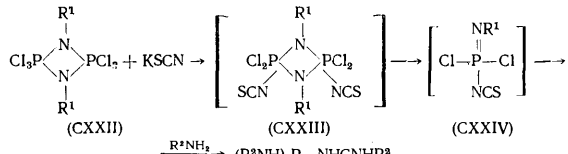
$$(C_6H_5O)_2P(O)NCS \gg (C_6H_5)_2P(O)NCS \approx (C_2H_5O)_2P(O)NCS > (C_2H_5)_2P(O)NCS > C_6H_5NCS.$$

The reactions are completed faster in acetone and dioxan than in CCl_4, which has been explained[180] by the influence of the unshared electron pairs of the oxygen atoms in the molecules of the first two solvents.

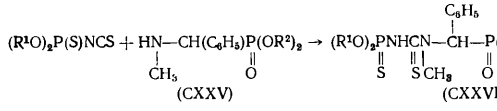
Optically active *N*-phosphorylated thioureas have been obtained by the reaction of amines with optically active phosphorylated isothiocyanates.[5,6,37,60] The reaction of the ^{32}P-labelled diphenylphosphinothioic isothiocyanate with the ε-amino-groups of the lysine side chains in proteins has been used to introduce a radioactive label into γ-globulin.[67] *N'*-hydantoinyl-*N''*-phosphorylthioureas have been obtained from the corresponding disubstituted 5-aminohydantoins and dialkyl phosphoroisothiocyanatidates and phosphoroisothiocyanatidothioates.[163]

The synthesis of thioureidophosphazoarenes (CXXI) via Scheme 21 by treatment of *NN'*-diarylhexachlorocyclophosphazans (CXXII) initially with KSCN and then with aromatic or heterocyclic amines in acetone at 0 °C has been described. It is suggested that the process proceeds via the intermediate (CXXIII) and (CXXIV):

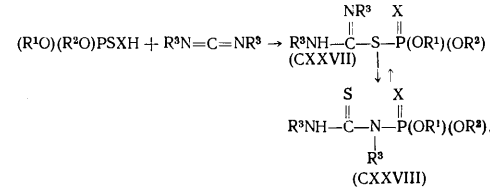
Scheme 21



Bisphosphorylated thioureas (CXXVI) are formed in the reactions of α-aminophosphonates (CXXV) with phosphoroisothiocyanatidothioates:[51]

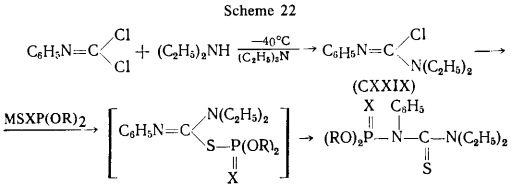


Together with the reactions of phosphorylated isothiocyanates with amines, other methods have also been used to synthesise *N*-phosphorylated thioureas, because the reactions of the amines are not free from certain limitations. In particular, thioureas in which the nitrogen atom linked to the phosphorus atom is fully substituted cannot be synthesised by these reactions. This can be achieved, for example, with the aid of the reactions of phosphorothioic and phosphorodithioic acids with carbodiimides.[140,192–199] The products of the addition of the thioacids of tetracoordinate phosphorus to the C–N bond in compounds (CXXVII), which have the isothiourea structure, can rearrange to *N*-(thio)phosphorylated thioureas (CXXVIII) in addition to undergoing other reactions. In certain cases (when R^3 = isopropyl or cyclohexyl) the rearrangement is reversible, but under the usual conditions the equilibrium is almost fully displaced towards the isomer (CXXVIII). The study of the stereochemistry of the conversion of *S*-phosphorylisothioureas into *N*-phosphorylthioureas[197,198] demonstrated the complete retention of the configuration at the phosphorus atom:



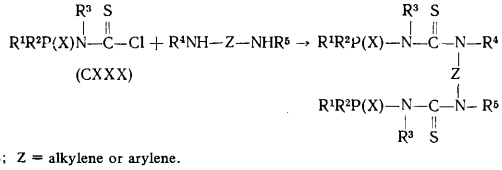
An analogous rearrangement of *S*-(thio)phosphorylated isothioureas to *N*-(thio)phosphoryl thioureas has been observed in the reaction of diethyl phosphorodithioic acid with cyanamide[48] and in exchange reactions of salts of dialkyl phosphorothioic and dialkyl phosphorodithioic acids with *NN*-diethyl-*N'*-phenylchloroformamidine (CXXIX) (Scheme 22):[107]

Scheme 22



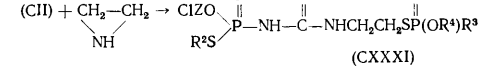
M = Na, K, NH_4; X = O or S.

Phosphoryl- and thiophosphoryl-thiocarbamoyl chlorides (CXXX) can condense with amines[155,156] and alkylene- and arylene-diamines[157] to form the corresponding mono- or bis-(thio)phosphorylthioureas:



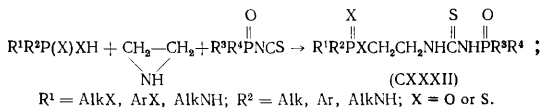
X = O or S; Z = alkylene or arylene.

Diphosphorylated thioureas (CXXXI) have been synthesised from *NS*-diphosphorylated dithiocarbamates (CI) and ethyleneimine:[200]



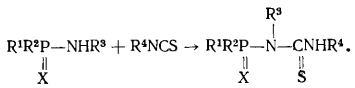
Analogous products (CXXXII) have been isolated in three-component reactions of the acid esters of phosphonic, phosphonodithioic, phosphonotrithioic, or phosphorodiamidodithioic acids with phorphoryl isothiocyanates and

ethyleneimine.[165,201,202] The corresponding *NS*-diphosphorylated thio- or dithio-carbamates of type (CII) are apparently formed in these reactions as intermediates:



$R^1 = AlkX, ArX, AlkNH;\ R^2 = Alk, Ar, AlkNH;\ X = O \text{ or } S.$

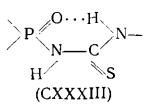
According to patent data,[155,156] phosphorylated thioureas can be obtained by adding the amides of tetracoordinate phosphorus acids to organic isothiocyanates:



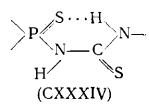
The addition of *cis*- and *trans*-2-amido-4-methyl-2-oxo-1,3,2-dioxaphosphorinanes to cyclohexyl isothiocyanate takes place in the presence of sodium hydride.[37] Diaminotetrakis(dimethylamino)cyclotriphosphazene reacts with phenyl isothiocyanate in boiling benzene to form a monosubstituted derivative of thiourea.[28]

2. The Properties of *N*-(Thio)Phosphorylated Thioureas

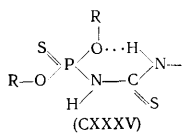
It has been established by IR spectroscopy[203] that *N*-phosphorylated and *N*-thiophosphorylated thioureas do not exhibit a tendency towards the thione–thiol tautomerism both in polar and in non-polar solvents. In a study of the concentration dependence of the IR spectra, it was found that these compounds are associated both in the crystalline state and in concentrated solutions as a result of the formation of intermolecular hydrogen bonds involving the P–NH, C=S, and P=S groups. In dilute solutions in CCl_4 an equilibrium is established between the self-associated species and their monomers. The intermolecular hydrogen bonds (CXXXIII), (CXXXIV), and (CXXXV) make a significant contribution to the stabilisation of the monomeric forms:



(CXXXIII)

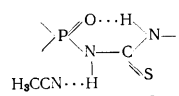


(CXXXIV)

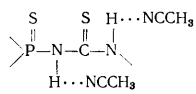


(CXXXV)

Heteroassociated 1:1 and 1:2 species arise in acetonitrile for the phosphoryl [compound (CXXXVI)] and thiophosphoryl [compound (CXXXVII)] derivatives respectively:

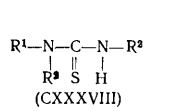


(CXXXVI)

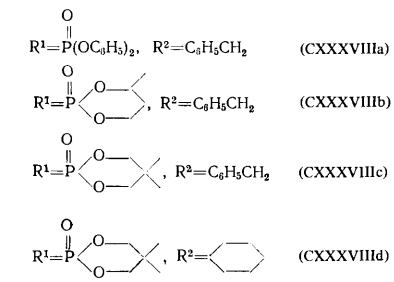


(CXXXVII)

The X-ray diffraction study of *NN'*-dibenzyl-*N*-diphenylphosphorylthiourea (CXXXVIIIa),[204] *NN'*-dibenzyl-*N*-(4-methyl-2-oxo-1,3,2-dioxaphosphorinanyl)thiourea (CXXXVIIIb),[198] *NN'*-dibenzyl-*N*-(5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinanyl)thiourea (CXXXVIIIc), and *NN'*-dicyclohexyl-*N*-(5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinanyl)thiourea (CXXXVIIId)[205] revealed significant structural and conformational differences between the dibenzyl derivatives (CXXXVIII, a–c) and the dicyclohexyl derivative (CXXXVIIId):



(CXXXVIII)



(CXXXVIIIa)

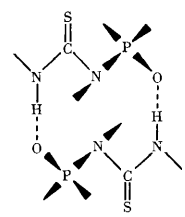
(CXXXVIIIb)

(CXXXVIIIc)

(CXXXVIIId)

In compounds (CXXXVIII, a–c) the sulphur and phosphorus atoms occupy virtually antiperiplanar positions about the SC–NP bond (torsional angle of about 160°). The thiourea fragment in the dibenzyl derivatives (CXXXVIII, a–c) is planar. A chelate six-membered ring is formed in these molecules via the intramolecular NH...O=P hydrogen bond.

The presence of the two bulky cyclohexyl substituents in the molecule of compound (CXXXVIIId) disturbs the planarity of the thiourea skeleton. The deviation of the phosphorus atom from the plane of the nitrogen and sulphur atoms in compound (CXXXVIIId) amounts to 1.435 Å while in compound (CXXXVIIIc) it is only 0.490 Å. The P–N–C–S torsional angle is 91°, so that the non-bonding S...P distance, amounting to 3.73 Å in compound (CXXXVIIId), is much shorter than in compound (CXXXVIIIc) (4.242 Å). The rotation about the PN bond in compound (CXXXVIIId) is restricted owing to the interaction of the α-protons of the cyclohexane ring with the phosphoryl oxygen; the rotation about the PN–CS bond is also hindered. The thiourea (CXXXVIIId) gives rise to the dimers (CXXXIX) in the crystalline state, which are stabilised by intermolecular hydrogen bonds:

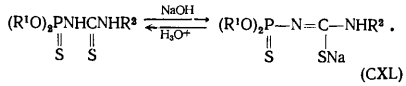


(CXXXIX)

The structural and conformational differences between the thioureas of types (CXXXVIII, a–c) and (CXXXVIIId) are also shown in the NMR spectra. The spin–spin coupling constants ^3J(P–N–C–H) for *NN'*-dicyclohexyl- and *NN'*-diisopropyl-phosphorylthioureas are unusually high (20.5 to 25.4 Hz) compared with other *N*-phosphorylated thioureas (9.5–10.0 Hz). For the thiophosphoryl derivatives, the difference between the ^3J(PH) is not quite so significant, but it does exist. On the basis of the invariance of the constants ^3J(PH) when the solvents are varied, the authors[199] concluded that the most stable conformations of the *NN'*-disubstituted phosphorylthioureas (CXXXVIII) are identical in the crystalline state and in solution.

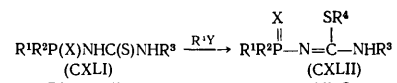
Like *N*-thiophosphoryldithiocarbamates, *N'*-substituted *N*-dialkylthiophosphorylthioureas are weak acids with $pK_a \cong 8.8$ (in an aqueous alcoholic medium) [51,176,203] and form water-soluble salts (CXL) with alkalies or alkali metal

alkoxides:[51]



(CXL)

Like *N*-(thio)phosphoryl(di)thiocarbamates, the thioureas (CXLI) are alkylated by various alkylating agents with formation of *S*-alkyl-*N*-(thio)phosphorylisothioureas (CXLII):[179,206–210]

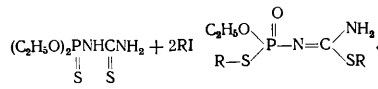


(CXLI) (CXLII)

R^4Y = AlkHal, AlkOTs, $AlkCHN_2$, Alk_2SO_4.

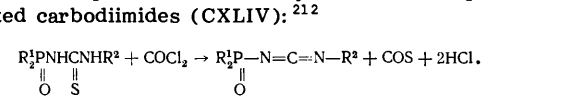
The alkylation is sometimes accompanied by the Pishchimuka rearrangement:[208]

Scheme 23



The interaction of *N*-(thio)phosphorylthiourea with Methylene Blue in 85% ethanol leads to the reduction of the dye to a substituted phenothiazine, thiourea dimerising under these conditions.[211]

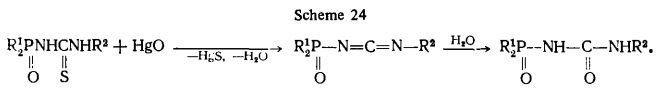
The reactions of the phosphorylthioureas (CXLIII) with phosgene in the presence of tertiary bases lead to phosphorylated carbodiimides (CXLIV):[212]



(CXLIII) (CXLIV)

The carbodiimides (CXLIV) can be obtained from compound (CXLIII) by desulphurisation with mercury(II) oxide in boiling benzene in accordance with Scheme 24. It is then essential to bind the water evolved, since otherwise the phosphorylated ureas (CXLV) are formed:[212]

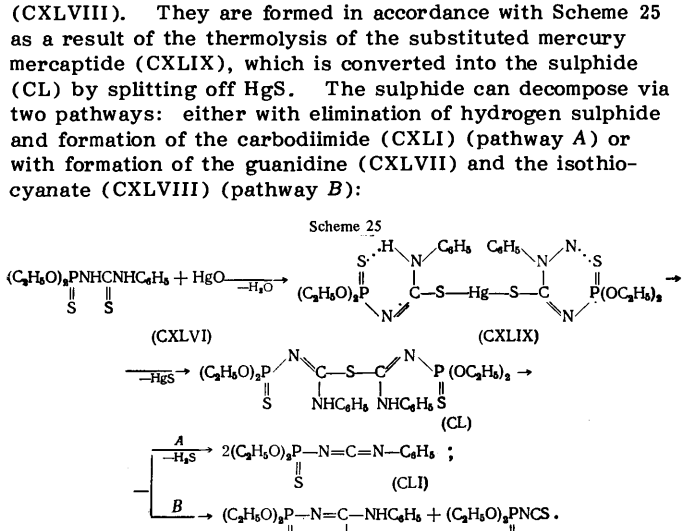
Scheme 24



(CXLIII) (CXLIV) (CXLV)

According to Grapov et al.[213], the yield of the thiophosphorylated carbodiimides is low when this method is used. The main products of the reaction of the thiourea (CXLVI) with mercury(II) oxide are compounds (CXLVII) and (CXLVIII). They are formed in accordance with Scheme 25 as a result of the thermolysis of the substituted mercury mercaptide (CXLIX), which is converted into the sulphide (CL) by splitting off HgS. The sulphide can decompose via two pathways: either with elimination of hydrogen sulphide and formation of the carbodiimide (CXLI) (pathway *A*) or with formation of the guanidine (CXLVII) and the isothiocyanate (CXLVIII) (pathway *B*):

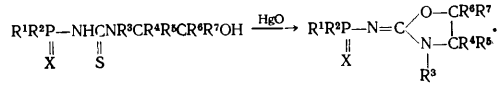
Scheme 25



(CXLVI) (CXLIX) (CL) (CLI) (CXLVII) (CXLVIII)

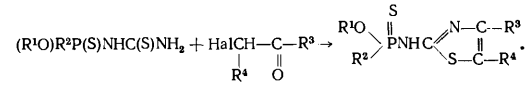
When *N*-phosphoryl- and *N*-thiophosphoryl-thiourea are heated with HgO in the presence of alcohols, mercaptans, and amines, the corresponding phosphorylated and thiophosphorylated isoureas, isothioureas, and guanidines are formed.[213,214]

The products of the addition of aminoalcohols to phosphorylated isothiocyanates (CLII) cyclise to *N*-phosphorylimino-oxazolidines (CLIII) under the influence of mercury(II) oxide with elimination of hydrogen sulphide:[215–219]



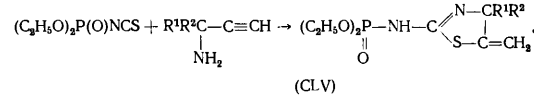
(CLII) (CLIII)

The reactions of thiophosphorylated thioureas with α-halogenoketones lead to the formation of phosphorus-containing aminothiazoles (CLIV):[220]



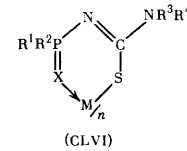
(CLIV)

Diethyl *N*-(2-thiazolinyl)phosphoramidates (CLV) are the products of the reaction of diethyl phosphoroisothiocyanatidate with substituted propargylamines:[221,222]



(CLV)

The molecules of phosphorylated thioureas contain several centres capable of forming a coordinate bond with metal ions. It has been reported in two reviews[1,21] that the formation of stable mono- or bi-ligand chelates of type (CLVI) is characteristic of these compounds. The complex formation reaction is accompanied by the displacement of one or two protons:

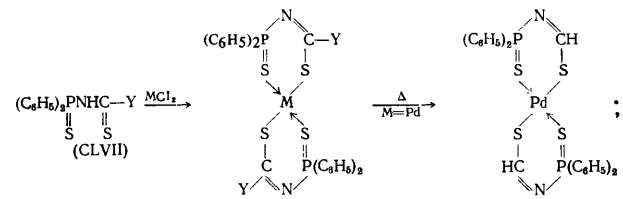


(CLVI)

X = O, S; M = Co(II), Ni(II), Cu(I); *n* = 1, 2

New data concerning the formation of complexes by *N*-(thio)-phosphorylthioureas with metal ions have been published.[51,150,152,156,175–178,186,223]

Ojima and co-workers[177,178] investigated the complex formation reactions between diphenylphosphinothioylthioureas (CLVII) and nickel(II), palladium(II), and cobalt(II) ions, which leads to the formation of 1 : 2 chelates having the structure (CLVIII):



(CLVII) (CLVIII) (CLIX)

Y = $N(CH_3)_2$, $N(C_2H_5)_2$, NHC_6H_5; M = Co(II), Ni(II), Pd(II).

In the reaction with palladium(II) ions (for R = NHC_6H_5), another chelate is isolated together with the complex (CLVIII) to which the structure (CLIX) was attributed on the basis of

IR spectroscopic, X-ray diffraction, and elemental analyses. The authors[178] believe that, when the complex (CLVIII) is heated, the ligand is partly destroyed, but the six-membered ring is retained.

The complexes with the nickel(II) and palladium(II) ions are diamagnetic at room temperature, which indicates their planar configuration. The IR and UV spectra confirm this. The cobalt(II) complexes are paramagnetic and have a tetrahedral configuration. On formation of complexes with copper(II) ions, the copper is reduced to the univalent state, but the reaction products could not be isolated in this instance.

A study of complex formation reactions of the thioureas (CLVII, R = phenylamino, *m*-tolylamino, α- and β-naphthylamino, or piperidinyl) with nickel(II) ions showed that the complexes have the 1:2 composition and in most cases have a planar structure.[186]

The formation of complexes by *N*-thiophosphorylthioureas with nickel, cobalt, mercury, and silver ions and the structures of the resulting chelates have been investigated[176,223] by spectrophotometric, potentiometric, IR spectroscopic, and ^{31}P NMR methods.

In view of the ability of *N*-thiophosphorylthioureas to form chelates which can be extracted from aqueous media by organic solvents, they can be used as extractants in analytical chemistry. Thus it has been shown[175,176] that many metal ions [Cu, Co, Ag, Cd, Au, Al, Mo, Ni, Gg, Ga, In, Bi, Pd, Pb, Zn, Mn(II), Tl, Ti] can be extracted from aqueous solutions of different acidity in the form of complexes with the aid of *NN*-diisopropyl-*N'*-phenylthiophosphorylthiourea. A procedure for the group concentration of microadmixtures of heavy metal ions in their chemical-spectroscopic analysis has been developed on the basis of the extraction properties of this compound.[175]

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The data presented show that phosphorylated isothiocyanates as well as *N*-phosphorylated monothio- and dithiocarbamates and thioureas, which are genetically related to the isothiocyanates, possess a broad spectrum of properties useful in practice. Presumably further studies in this interesting field of organophosphorus chemistry will be directed towards a deepening of our knowledge of the structure and properties of these important and useful compounds, towards the search for new possibilities in their practical application, and also towards the development of the most technological processes for their synthesis.

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The Synthesis and Properties of Silicon-, Germanium-, Tin-, and Lead-containing s-Triazines

A.S.Gordetsov and Yu.I.Dergunov

Published data on the methods of synthesis and properties of s-triazines containing group IVb elements have been summarised and systematised. The reaction mechanisms have been discussed, and various aspects of the practical application of s-triazines examined.
The bibliography contains 222 references.

CONTENTS

I. Introduction 1227
II. Methods of synthesis 1227
III. Physicochemical properties and structure 1236
IV. Chemical properties 1237
V. Practical applications 1241

I. INTRODUCTION

The first papers on the synthesis of derivatives of s-triazine appeared about the middle of last century. Thousands of compounds of this class have now been prepared and studied, and in a number of cases have found practical applications. The interest in these compounds is related to their high inertness and chemical and thermal stability, which result from the unique electronic structure of the ring, and also to the high biological activity of some derivatives. Most published data on the methods of preparation, structure, properties, and applications of organic s-triazines and their salts have been summarised in a monograph[1] and reviews,[2,3] but there has been practically no systematisation of published data on their hetero-organic analogues, which are attracting increasing interest.

The aim of the present work was to systematise published data on the synthesis, reactivity, physicochemical properties, and applications of silicon-, germanium-, tin-, and lead-containing derivatives of s-triazine in which the element-containing fragments are joined directly to the ring.

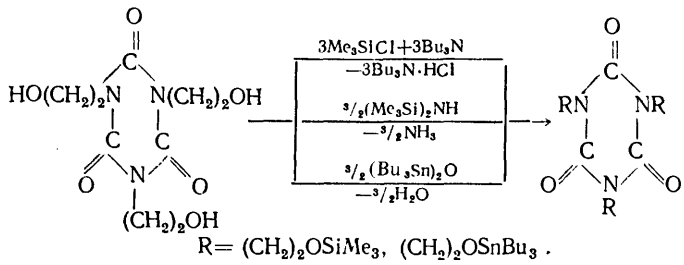
Papers dealing with carbofunctional s-triazines are not considered in detail, and are used only for comparison with data on the main group of compounds being examined, although the information on these compounds is given in full. The review includes material published in monographs, journal articles, and patents up to June 1984.

II. METHODS OF SYNTHESIS

1. The Reaction of s-Triazines with Hetero-organic Compounds

The first representative of this group of compounds, tris-(β-trimethylsiloxyethyl) isocyanurate, was synthesised in high yield by the reaction of tris(β-hydroxyethyl) isocyanurate with trimethylchlorosilane in the presence of Bu_3N [4] (scheme 1):

Scheme 1

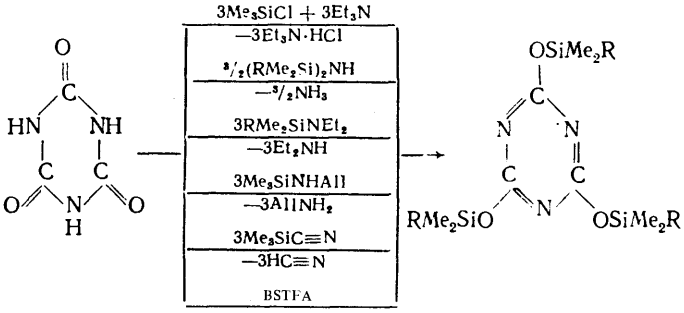


R= $(CH_2)_2OSiMe_3$, $(CH_2)_2OSnBu_3$.

The organotin analogue of the same isocyanurate was obtained in quantitative yield by the reaction with hexabutyldistannoxane,[5,6] and also by the reaction of $(Bu_3Sn)_2O$ with bis(β-iodoethyl) β-hydroxyethyl isocyanurate (yield 15%) and of tris(tributylstannyl) isocyanurate with ethylene oxide.[5]

An attempt to silylate isocyanuric acid in an autoclave at 350 °C by a shceme analogous to scheme 1 was initially unsuccessful,[7] but the use of dimethylformamide as solvent and of triethylamine (Et_3N) as HCl acceptor gave tris(trimethylsilyl) cyanurate in 74% yield[8-11] (scheme 2):

Scheme 2



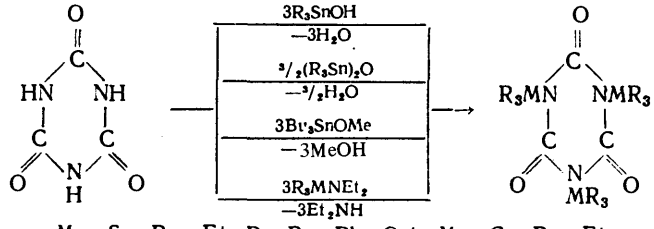
All = $-CH_2-CH=CH_2$, R = H, Me.

This cyanurate and its dimethylsilyl analogue were also obtained using the corresponding triorganosilylamines (scheme 2),[8-14] trimethylsilyl cyanide,[15] or N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA).[16]

The most promising reactions, because of their high yields and the purity of the desired products, are the reactions of isocyanuric acid with hexamethyl- or tetramethyldisilazanes (ammonium sulphate catalyst). The organosilicon cyanurates obtained can be purified by vacuum distillation, but increase in the distillation temperature or the presence of chlorine-containing impurities leads to their thermal decomposition.[12-14,17]

The first organotin s-triazines were obtained by Stamm,[18-20] again by the direct metallation of isocyanuric acid by tin-containing oxides and hydroxides (100–160 °C); with evacuation [scheme (3)]:

Scheme 3



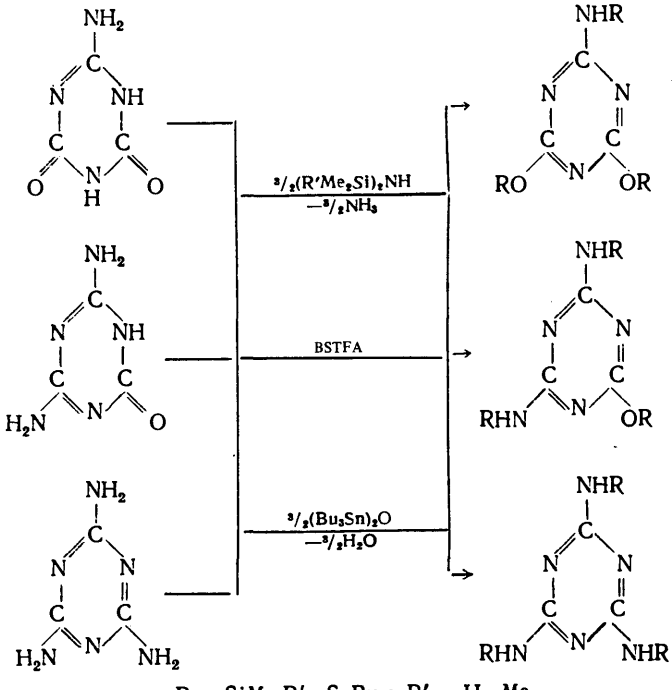
M = Sn, R = Et, Pr, Bu, Ph, Cct; M = Ge, R = Et.

The same method was later used to synthesise tris-substituted isocyanurates of triethyl- and tripropyltin.[21-23] The synthesis of these products by the reaction of cyanic acid with organotin oxides and hydroxides has been reported.[24] Under the given conditions (120–190 °C), however, the process probably involves the formation of isocyanuric acid, followed by reaction according to scheme 3.

The reaction of isocyanuric acid with methoxy- and diethylaminostannanes or diethylaminogermane gives the corresponding highly pure hetero-organic isocyanurates.[8,9,25]

Tris(organosilicon)- and tris(organotin)-derivatives of amino(hydroxy)-s-triazines were obtained similarly. Thus the reaction of the latter with hexamethyl- and tetramethyldisilazanes (HMDS and TMDS respectively) or BSTFA gave tris(trimethylsilyl)- and tris(dimethylsilyl)ammelide, -ammeline, and -melamine[9,11,16,26,27] (scheme 4):

Scheme 4



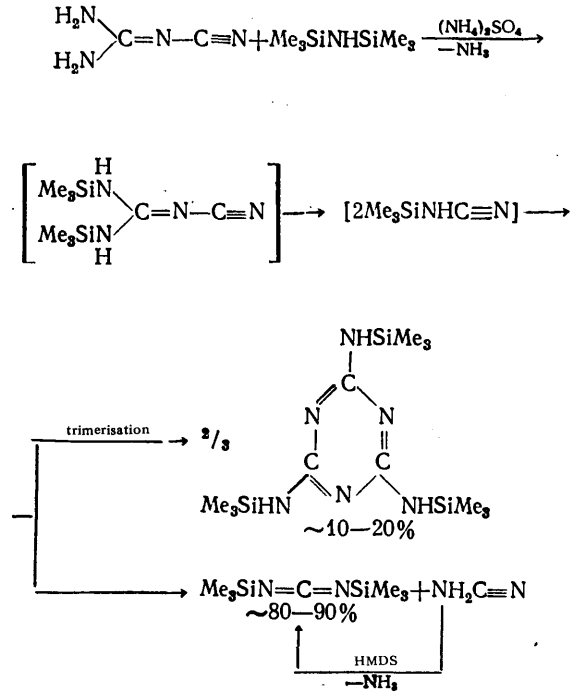
R = $SiMe_2R'$, $SnBu_3$; R' = H, Me.

The same heterocyclic compounds react with hexbutyldistannoxane to give the corresponding organotin compounds in good yield,[9,28] but they do not react with hexaethyldigermoxane.

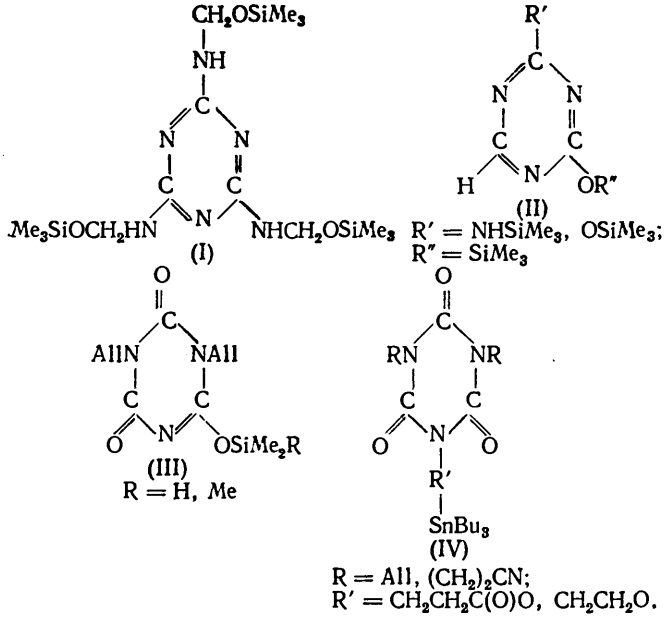
Silylation using HMDS or TMDS (ammonium sulphate catalyst) becomes increasingly difficult in the series isocyanuric acid–ammelide–ammeline–melamine, that is as the carbonyl groups are replaced by NH_2 groups. Thus the silylation of the first member of the series takes not more than 1–2 h, and a catalyst is not necessary, whereas tris-silicon-substituted melamine is obtained in 70% yield only after heating the reagents for 60 h in the presence of $(NH_4)_2SO_4$.

Other workers[29] who repeated this synthesis (H_2SO_4 catalyst, 140 °C, 6 h) were able to isolate only 2,4-bis(trimethylsilylamino)-6-amino-s-triazine in 35.5% yield, and the tris-substituted analogue was not obtained. There is no doubt that tris(trimethylsilyl)melamine exists, however, since it has been isolated in large quantities and identified as a by-product in the extended treatment of bis(trimethylsilyl)-carbodi-imide by the published methods.[30-33] A scheme for the formation of an organosilicon derivative of melamine has been proposed[33] (scheme 5):

Scheme 5

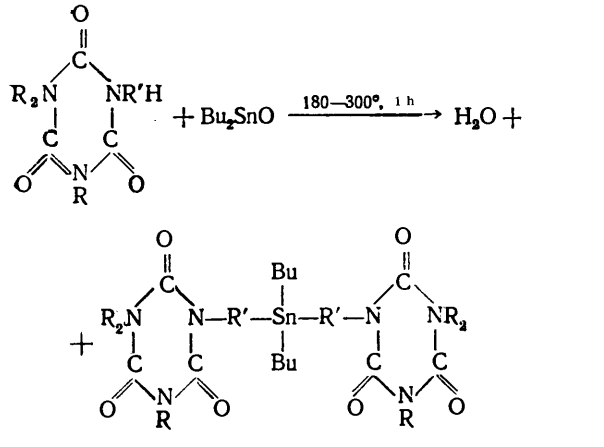


Reactions analogous to those of schemes 1–4 can also be used to obtain silylated derivatives of methylol- and organo-substituted melamines (for example compound (I),[34-37] amino-(hydroxy)-s-triazines (II),[38-42] organosilicon and organotin diallyl or dicyanoethyl isocyanurates (III), (IV),[5,6,43-45] and other compounds, frequently used as intermediates in organic synthesis:



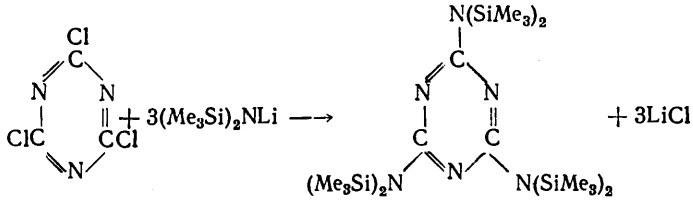
Organotin bis-triazine derivatives are formed according to a scheme which does not differ fundamentally from scheme 3 [5,6,46,47] (scheme 6):

Scheme 6



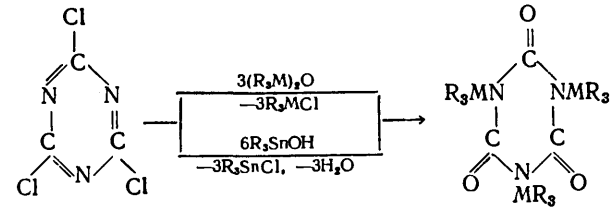
Mono-, di-, and trimethylsilyl derivatives of melamine can be synthesised using cyanuric chloride as the original s-triazine, and hexakis(trimethylsilyl)melamine has been obtained in low yield by the reaction of the latter with $(Me_3Si)_2NLi$ [29, 32,48–50] (scheme 7):

Scheme 7



Cyanuric chloride has also been used to obtain other hetero-organic s-triazines. Thus the organogermanium s-triazine tris(triethylgermyl) isocyanurate was first synthesised according to scheme 8 by heating a mixture of the reagents in dibutyl ether for a long time. The yield was 73%. [51]

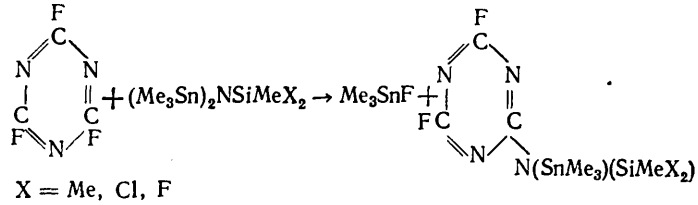
Scheme 8



M = Ge, R = Et; M = Sn, R = Et, Bu, $PhCH_2$— .

Cyanuric chloride reacts similarly with triethyltin and tribenzyltin hydroxides and hexabutyldistannoxane. [51] The use of cyanuric chloride to obtain various carbofunctional organosilicon s-triazines [48,52–57] (including trimethylsilylethynyl, [52] trimethylsilylphenyl, [53] and other derivatives) and triazine-containing polysiloxanes [58–66] has also been described. Cyanuric fluoride can be used instead of cyanuric chloride. Thus the reaction of cyanuric fluoride with mixed organosilicon–tin amines has been used to synthesise a number of corresponding mono-substituted s-triazines [67] (scheme 9):

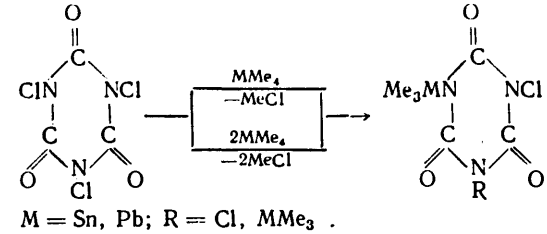
Scheme 9



X = Me, Cl, F

Trichloroisocyanuric acid has been used to synthesise hetero-organic compounds of this class. A method has been described [68] for obtaining mono- and di-substituted organotin isocyanurates and a dialkyltin bis-isocyanurate derivative using the above chlorine-containing heterocyclic compound. The same method was used to prepare the only mono- and di-substituted organolead s-triazines which have been obtained up to the present, namely dimethylplumbyl dichloroisocyanurate and bis(trimethylplumbyl) chloroisocyanurate [68] (scheme 10):

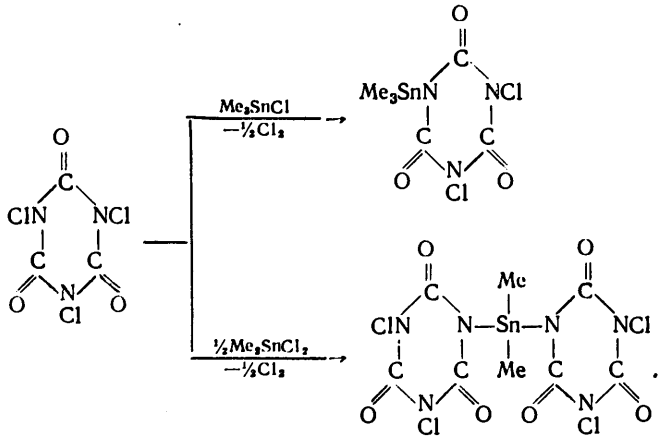
Scheme 10



M = Sn, Pb; R = Cl, MMe_3 .

If the metallating reagent contains a chlorine atom, molecular chlorine is liberated instead of methyl chloride. For example, in the case of trimethylchloro- or dimethyldichlorostannanes, the products were chlorine and trimethylstannyl dichloroisocyanurate or bis(di-chloroisocyanurato)dimethylstannane respectively (scheme 11):

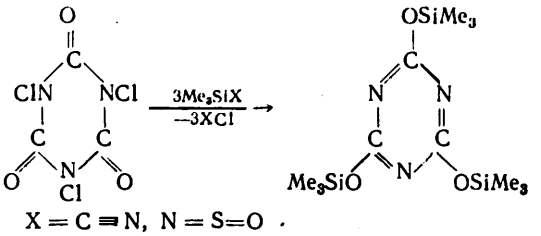
Scheme 11



The analogous organosilicon derivatives, trimethylsilyl and dimethylsilyl dichloroisocyanurates, have been described.[69]

The reaction of trichloroisocyanuric acid with trimethylsilyl cyanide and sulphinyl imide,[15] in which exchange of trimethylsilyl fragments and chlorine atoms takes place to give tris-(trimethylsilyl) cyanurate, was studied later (scheme 12):

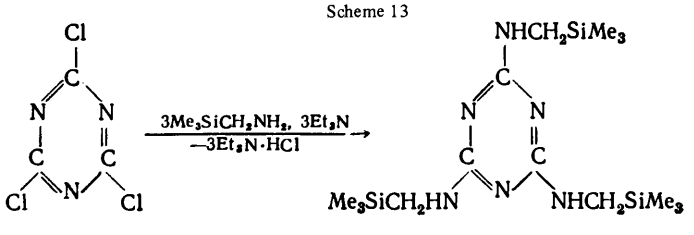
Scheme 12

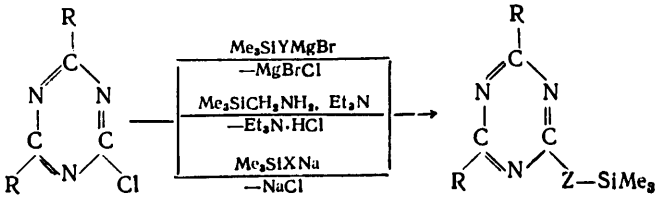


X = C≡N, N = S=O .

The routes by which cyanuric chloride and other halogenotriazines are converted into their hetero-organic analogues are extremely varied. For example, the above trimethylsilylethynyl[52] or trimethylsilylphenyl[53] heterocycles are obtained using a Grignard reagent, and a number of carbofunctional derivatives are obtained by the reaction with Me_3SiCH_2L (L = NH_2, ONa, SNa; boiling benzene, 6 h)[51] (scheme 13):

Scheme 13



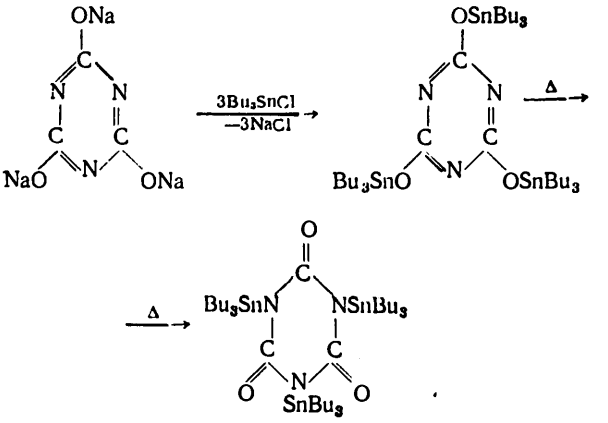


R = Cl, Y = Z = —C≡C—, —C_6H_4—; R = Ph,
X = Z = CH_2O, CH_3S; R = Ph, NH_2, Z = CH_2NH.

In contrast to this scheme, the reaction of cyanuric chloride with sodium triethylsilanolate (160–200 °C, 1 h, without solvent) gave not tris(triethylsilyl) cyanurate but its decomposition product Et_3SiNCO and NaCl.[17]

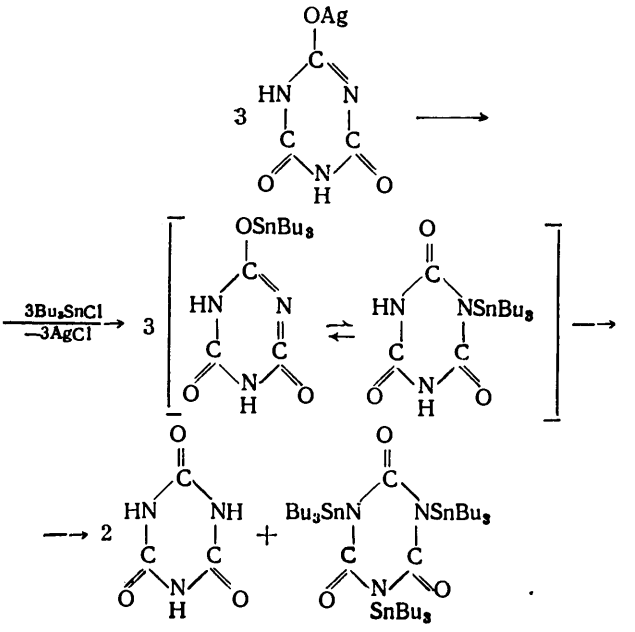
Sodium chloride is also formed in the reaction of sodium isocyanurate with tributylstannyl chloride (50 °C, 5 h), and the yield of the desired product, tris(tributylstannyl) isocyanurate, reaches only 18%.[51] The authors proposed and confirmed by infrared (IR) spectroscopy a reaction scheme involving the intermediate formation of the comparatively unstable cyanurate isomer (scheme 14):

Scheme 14



The transformations involving tributylstannyl chloride and various salts of isocyanuric acid were studied in more detail in Ref.70. The addition of moist solvents (acetonitrile, dimethylformamide) to the reaction system increases the yield of the Sn-s-triazine to 37%. In dry dimethylformamide the yield was 15%. The influence of moisture is attributed to the partial hydrolysis of the original salt to give isocyanuric acid, which is then stannylated by the hexabutyldistannoxane formed to give the tris-substituted isocyanurate according to scheme 3. The reaction of tributylstannyl chloride with thoroughly dried monosilver isocyanurate, contrary to expectations, also gave tris(tributylstannyl) isocyanurate (yield 79%) (scheme 15):

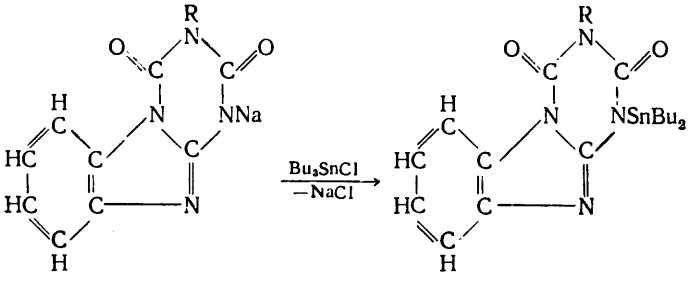
Scheme 15



Treatment of the unseparated reaction mixture with hexabutyldistannoxane gave an additional quantity of organotin isocyanurate. Similar treatment of monocalcium isocyanurate gave the same product in 70% yield.

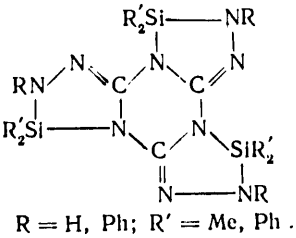
In contrast to this, the monosodium salts of triazine benzimidazoles react with tributylstannyl chloride to give the corresponding mono-substituted organotin compounds[71,72] according to scheme 16:

Scheme 16



R = $(CH_2)_5CN$, $(CH_2)_5CO_2Me$, $(CH_2)_5CO_2Et$, NMe_2, Alk, Ar etc.

A series of substituted organosilicon triazoles containing triazine rings were obtained similarly.[73]

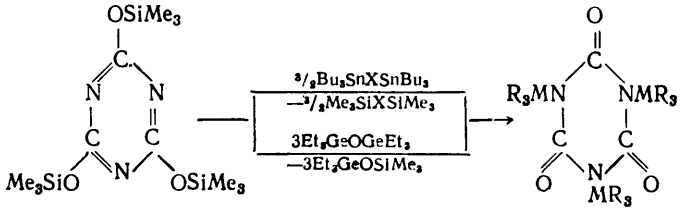


R = H, Ph; R′ = Me, Ph.

A promising method for obtaining hetero-organic s-triazines is provided by remetallation, which gives high yields and pure products. The chief condition for success is the continuous vacuum distillation of the volatile products.

This method was used to synthesise tris(triethylgermyl) and tris(tributylstannyl) isocyanurates; the substrate used was tris(trimethylsilyl) cyanurate, and hexaethyldigermoxane was remetallated to $Et_3GeOSiMe_3$ [9,33,74] (scheme 17):

Scheme 17

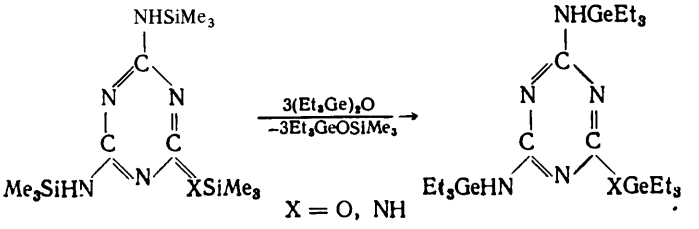


M = Ge, Sn; X = O, N=C=N.

The remetallation is reversible, and without evacuation gives a mixture of the starting materials and final products[75] (see scheme 43 in section IV).

By analogy with scheme 17, the corresponding organosilicon compounds gave for the first time tris-substituted organogermanium derivatives of ammeline and melamine[9,28] (scheme 18):

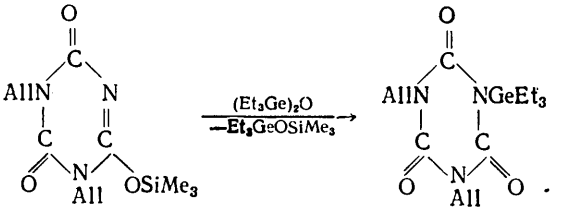
Scheme 18



X = O, NH

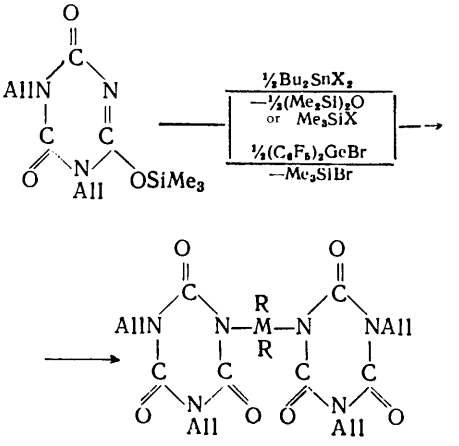
Remetallation also proved successful for the synthesis of triethylgermyl diallyl isocyanurate, since diallyl isocyanurate undergoes practically no direct reaction with hexaethyldigermoxane (200 °C, yield <5%)[43] (scheme 19):

Scheme 19



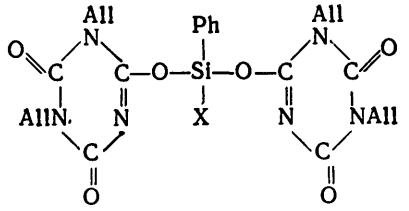
This method has been used to synthesise a number of hetero-organic derivatives of polydiallyl isocyanurates. Thus the reaction of two moles of trimethylsilyl diallyl isocyanurate with dichloro-, dibromo-, or dimethoxydibutylstannanes or dibutylstannoxane under comparatively mild conditions (100–120 °C, 0.5 h) gave bis(diallyl isocyanurato)dibutylstannane[46,76] according to scheme 20:

Scheme 20

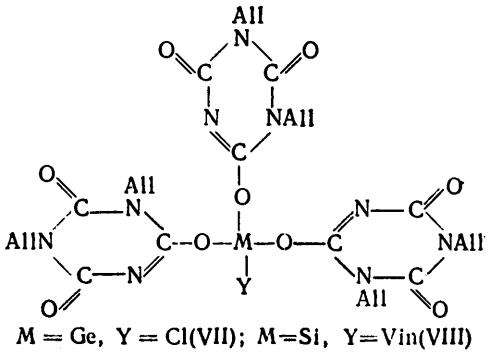


X_2 = O, $O(Me)_2$, Cl_2, Br_2; M = Ge, R = C_6F_5; M = Sn, R = Bu

The use of the corresponding hetero-organic halides and reagent ratios gave quantitative yields of bis(diallyl isocyanurato)methylphenyl- and -diphenylsilanes [compounds (V) and (VI)] and also tris(diallyl isocyanurato)chlorogermane and -vinylsilane (VII) and (VIII):[76]



X = Me(V), Ph(VI)

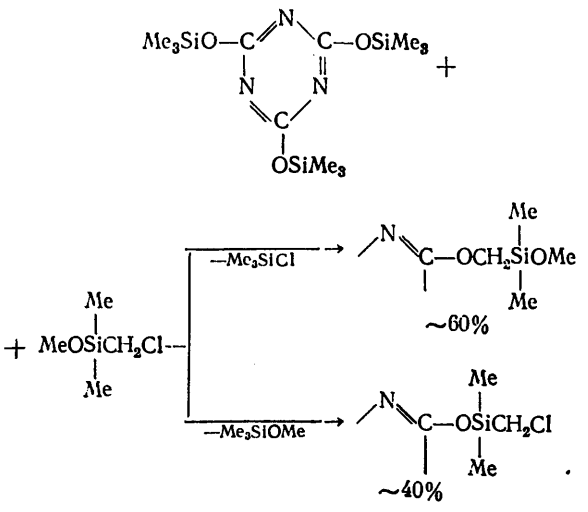


M = Ge, Y = Cl(VII); M=Si, Y=Vin(VIII)

It should be emphasised that organogermanium s-triazines are becoming accessible as a result of remetallation, since the most widely encountered starting materials, namely isocyanuric acid, ammelide, ammeline, melamine, and their many derivatives do not react with hexaethyldigermoxane under real conditions. The use of other germylating agents gives low yields of product.[9]

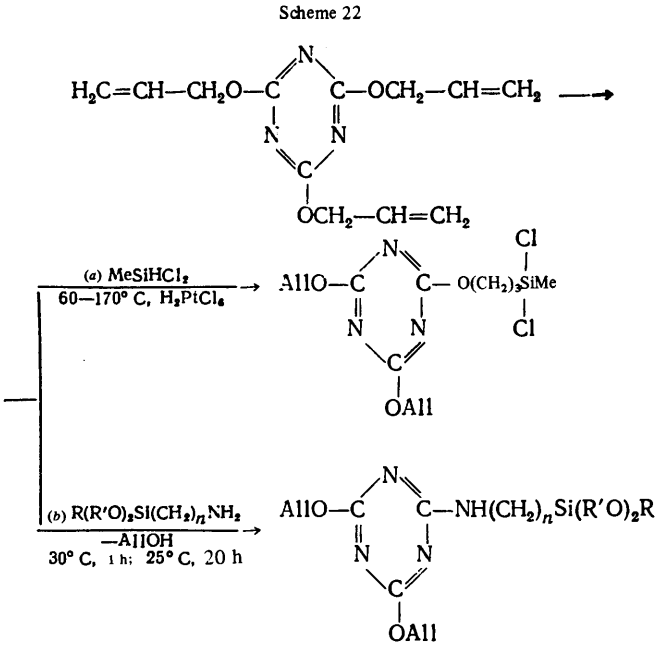
Tris(trimethylsilyl) cyanurate can react with α-chloromethylsilanes such as $(MeO)Me_2SiCH_2Cl$, $(EtO)_2MeSiCH_2Cl$, $(EtO)_3SiCH_2Cl$, etc. both in the direction of resilylation to give the alkoxytrimethylsilane and in the direction of silicoalkylation to give trimethylchlorosilane. This gives a mixture of organosilicon cyanurates containing two types of substituent in different combinations in the triazine ring[48] (scheme 21):

Scheme 21



Analogous compounds can also be obtained by the hydrosilylation of triallyl isocyanurate by chlorohydrosilanes, which, depending on the reagent ratio and the reaction conditions, gives the products of mono-, di-, and tris-addition, for example according to scheme 22a:[48]

Scheme 22



R = Me, R'O; R' = Me, Et; n = 2,4 .

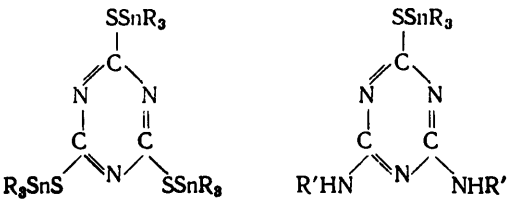
The same original s-triazine on partial ammonolysis under the influence of silylamines such as $R(R'O)_2Si(CH_2)_nNH_2$ is converted into the corresponding mono-substituted aminosilyl derivatives (scheme 22b).[77,78]

Hydrosilylation has also been used to prepare fluorosilicone-triazine polymers.[79-82]

Here it may be noted that the s-triazines synthesised according to schemes 21 and 22 [49,77,78,83] are as yet the only carbofunctional cyanurates, since other known analogues of this series exist in the oxo-form. In particular, Berger[84-87] showed by IR and NMR spectroscopy that the carbofunctional mono-, di-, and trialkyoxyorganosilicon heterocycles of this class, obtained by the reaction of triallyl isocyanurate with alkoxyhydrosilanes (100 °C, H_2PtCl_6), are isocyanurates.

A carbofunctional oxo-compound, tris[β-trimethylsilyl)-propionyl] isocyanurate, was synthesised by the reaction of tris(trimethylsilyl) cyanurate with β-(trimethylsilyl)propionyl chloride[17] (see scheme 39b, section IV).

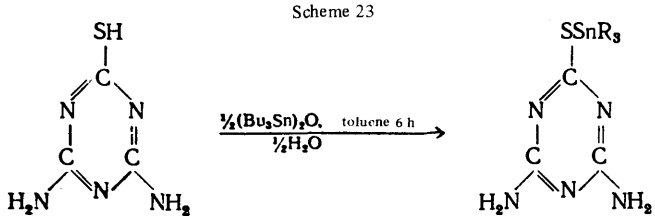
Sulphur-containing derivatives of organotin s-triazines have been obtained in good yields by the reaction of the appropriate thio-derivatives with various metallating agents according to schemes analogous to schems 1–4.[88-92] Examples of these compounds are tris[trialkyl(aryl)stannyl] trithiocyanurates and substituted trialkyl(aryl)stannylthioammelines



R = Pr, Bu, Ph, $PhCH_2$; R' = Et, Pr, iso-Pr, Bu, All, $MeO(CH_2)_2$, $MeO(CH_2)_3$ etc.

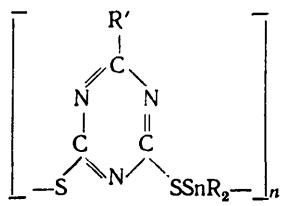
Unlike ammeline, thioammeline can undergo selective stannylation of the thiol group (scheme 23):[88]

Scheme 23



R = Pr, Bu, Ph, $PhCH_2$.

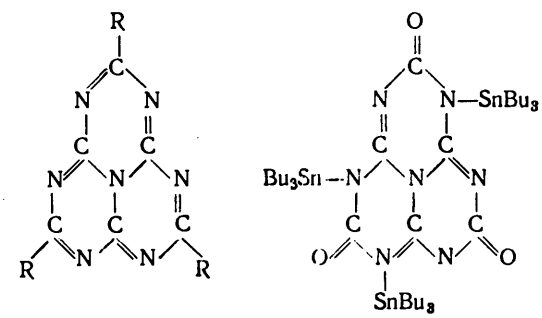
The reaction of thiotriazines or their sodium salts with dialkylstannoxanes and dichlorostannanes respectively gave oligomeric and polymeric s-triazine derivatives:[93]



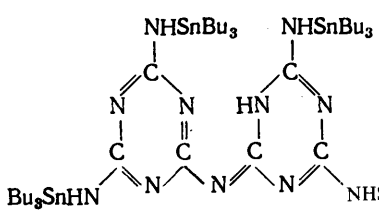
R = Me, Bu, Oct, Ph; R′ = PhO, PhNH, EtNH, Et_2N, MeO etc.; n = 5—293 .

In addition to the data on organosilicon sulphur-containing s-triazines given in scheme 13,[57] data on the preparation and uses of a number of their analogues have also been published.[94,95]

This group of methods can also be used to synthesise condensed and other complex hetero-organic systems containing s-triazine rings. Thus the reaction of hexabutyldistannoxane with cyameluric acid, melem, and melam gives tris-(tributylstannyl) cyamelurate, tris(tributylstannyl)melem, and tetra(tributylstannyl)melam respectively.[27,96,97] HMDS has been used to synthesise tris(trimethylsilyl) cyamelurate in high yield, but melem and melam do not undergo this reaction.



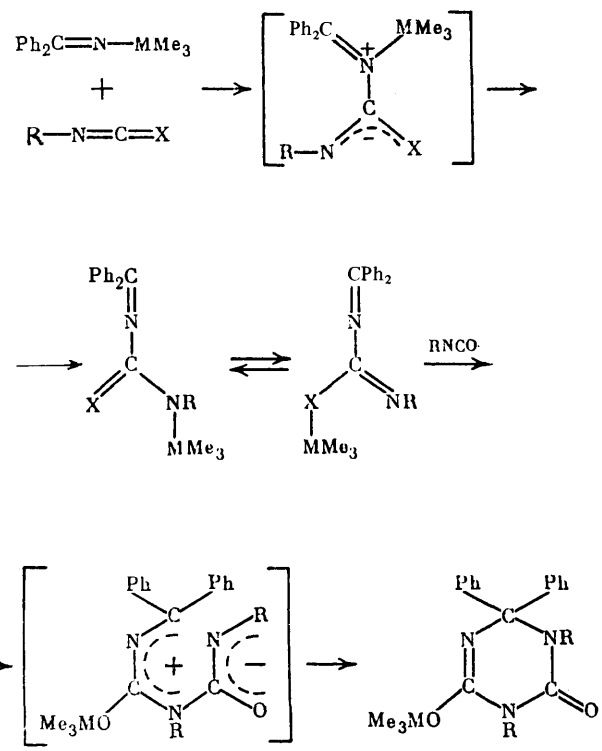
R = $OSiMe_3$, $NHSnBu_3$



2. The Cyclo-addition of Isocyanates to Substances with C=N Bonds

An extremely interesting and original method for obtaining hetero-organic s-triazines is provided by the cyclo-addition of isocyanates to the double bonds of nitrogen-containing hetero-organic compounds. In this case the s-triazine ring is formed in the reaction, and is not introduced into the system in the "prepared" form. Thus in the reaction of isocyanates with organosilicon and organotin derivatives of ketimines, a two-stage process gives the corresponding hetero-organic s-triazines (the reaction conditions are different for different M, R, and X)[98—100] (scheme 24):

Scheme 24



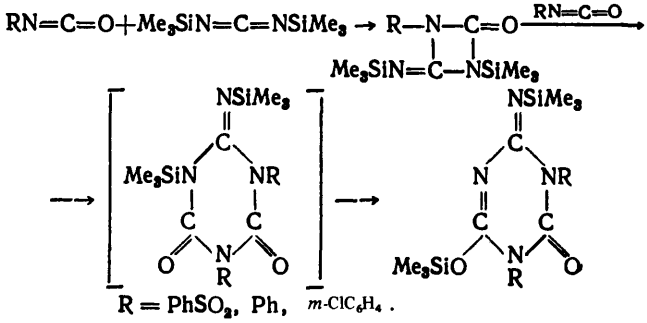
M = Si, Sn; R = Me, Ph; X = O, S .

In the first stage, the isocyanate is inserted at the element—nitrogen bond; the 1 : 1 adduct exists in two tautomeric forms (in the case of isocyanate the reaction is complete at this stage). In the second stage the next isocyanate molecule undergoes cyclo-addition with the 1 : 1 adduct.

The formation of similar s-triazines as intermediate compounds has been established in the reaction of $Ph_2C{=}N{-}S(O){-}PhSiMe_3$ with methyl isocyanate or $Cl_3CC{\equiv}N$.[101]

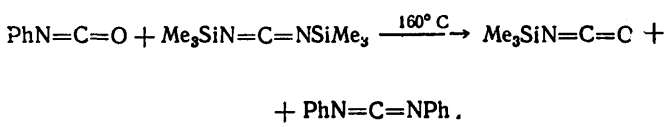
The reactions of isocyanates with organosilicon, -germanium, and -tin carbodi-imides is characteristic. The reaction of benzenesulphonyl isocyanate with bis(trimethylsilyl)carbodi-imide takes place on heating to 100—150 °C to give, depending on the conditions, four- or six-membered silicon-containing heterocycles according to scheme 25:[32,33,102]

Scheme 25



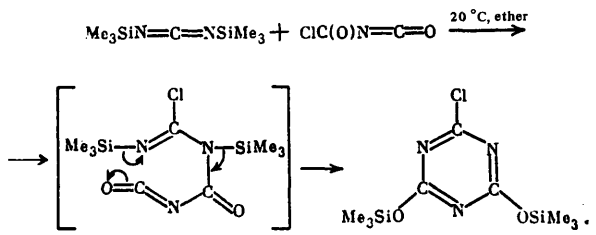
A similar scheme was proposed for the reaction of isocyanates with organic carbodi-imides.[103,104] The corresponding reactions of phenyl and *m*-chlorophenyl isocyanates take place under more severe conditions (190–250 °C, 3 h) to give as main products the corresponding organo-silicon s-triazines (yields 82–90%).[8,17,32,33,105] According to Ref. 106, the reaction of PhNCO with bis(trimethylsilyl)carbodi-imide with distillation of the volatile product (Me_3SiNCO) takes place as an exchange reaction, but no experimental proof was given (see scheme 26):

Scheme 26



In contrast to schemes 25 and 26, chloroformyl isocyanate reacts with bis(trimethylsilyl)carbodi-imide at a reagent ratio of 1:1 under mild conditions to give 2,4-bis(trimethylsiloxy)-6-chloro-1,3,5-triazine in 64% yield according to scheme 27:[32,107]

Scheme 27

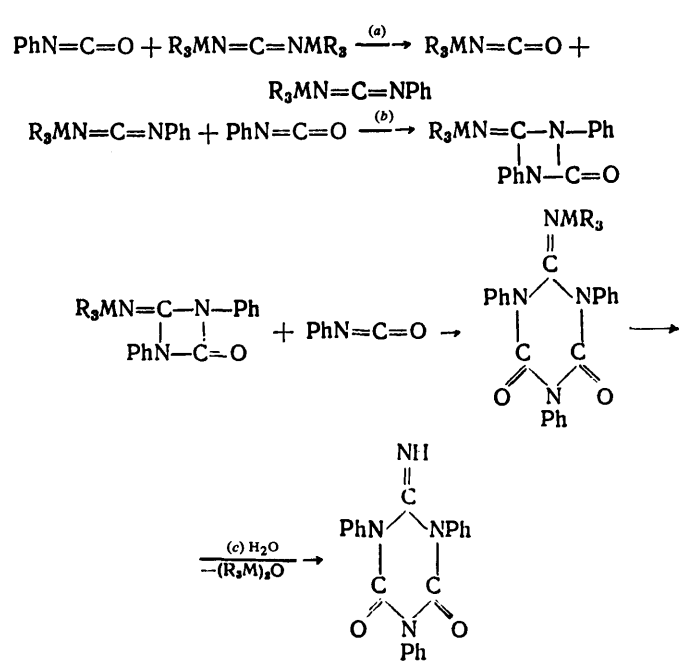


The scheme shows that the reaction begins with the electrophilic addition of isocyanate at the C=N bonds of the carbodi-imide. The product undergoes cyclisation with simultaneous migration of the Me_3Si groups from the nitrogen to the carbon atoms.

The reaction of the same isocyanate with Me_3SiNSO, instead of the expected OCN–CO–NSO and Me_3SiCl, gives tris(trimethylsilyl) cyanurate (yield 84%) and $(ClCONSO)_x$.[15]

Organogermanium and organotin s-triazines are also formed by the three-stage reaction of phenyl isocyanate with bis(tributylstannyl)carbodi-imides (scheme 28).[32,33,105,108]

Scheme 28

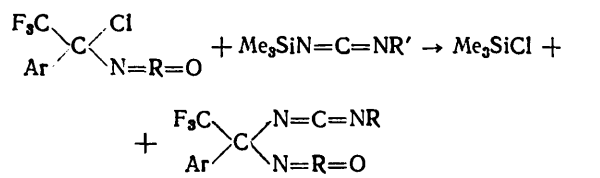


M=Ge, R=Et; M=Sn, R=Bu.

The scheme was confirmed by the IR spectra of the reaction mixtures and identification of the hydrolysis products. For example, heating phenyl isocyanate with $Bu_3SnN{=}C{=}NSnBu_3$ in the ratio 3:1 with subsequent hydrolysis of the reaction mixture gave 1,3,5-triphenyl-2-imino-4,6-dioxo-1,3,5-triazine in 61% yield. The last compound can be formed only by the hydrolytic splitting of the SnN bond of the corresponding organotin heterocycle (scheme 28c).[32,33,108]

In the case of $PhSO_2NCO$, scheme 28 is not realised, and germanium or tin s-triazines are not detected among the reaction products. The reaction involves exchange, and can be illustrated by a scheme analogous to schemes 26 and 28a. A similar result was established in a study of the reaction of unsymmetrical organosilicon carbodi-imides with α-chloroisocyanates according to scheme 29:[109–111]

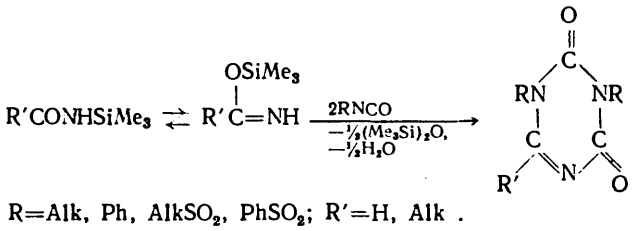
Scheme 29



R=C, S; Ar=Ph, *p*-MeC_6H_4, *p*-ClC_6H_4; R'=Ph, COOEt.

Cyclo-addition involving trimethylsilylformamides and isocyanates, leading to the intermediate formation of the corresponding organosilicon s-triazines, has been used to prepare their organic analogues, which are not readily obtainable[112] (scheme 30):

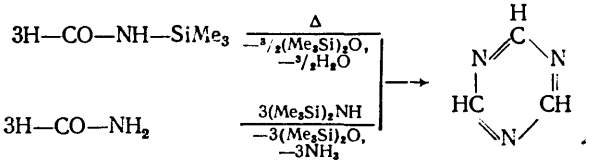
Scheme 30



R=Alk, Ph, $AlkSO_2$, $PhSO_2$; R'=H, Alk .

A similar process apparently forms the basis of the synthesis of s-triazine according to scheme 31:[113]

Scheme 31



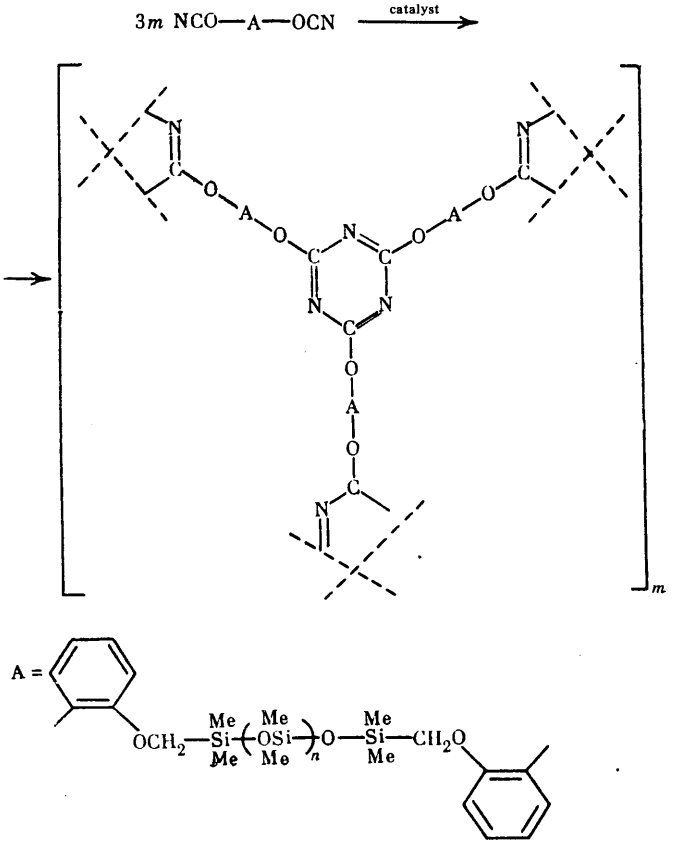
In contrast to the previous systems the analogous reactions of carbofunctional organosilicon imines give organosilicon s-triazines stable under ordinary conditions. Thus $Me_3Si(CH_2)_2C(OEt)=NH$ has been used to synthesise 2,4,6-tris-[β-(trimethylsilyl)ethyl]-1,3,5-triazine in quantitative yield.[114] The reaction of aminosilanes $R_3Si(CH_2)_3NH_2$ (R = Me, Et, Bu, EtO) with formaldehyde or paraform gave a number of other carbofunctional organosilicon analogues of the latter.[115–118] The aminosilane apparently first reacts with CH_2O by an A_N–E mechanism to give Schiff bases $R_3Si(CH_2)_3N=CH_2$, which subsequently trimerise to the corresponding s-triazines.

The addition of formaldehyde to trimethylisocyanatosilane gave as final product tris-[(trimethylsilyloxy)methyl] isocyanurate instead of its monomer $Me_3SiOCH_2N=C=O$ (CH_2O was bubbled through Me_3SiNCO at 80–83 °C.[119]

The formation of isocyanurates was also observed in the preparation of carbofunctional and organosilicon isocyanates by the reactions of KOCN with chlorine-containing siloxanes in dimethylformamide (DMF).[120–122] The improvement of the method has been protected by a series of patents devoted to the synthesis of carbofunctional s-triazines by heating mixtures of metal cyanates with various organosilyl halides in aprotic solvents (3–10 h, 90–140 °C, yield 90–95%).[123–130]

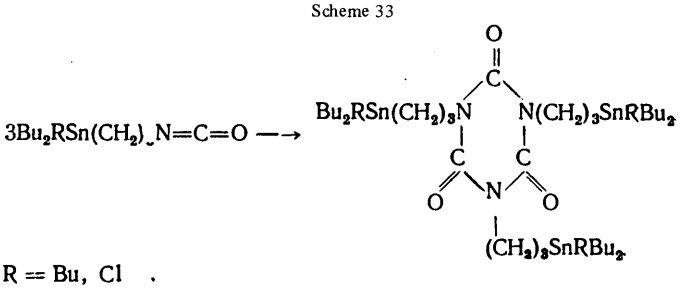
The trimerisation of isocyanates such as $Me_3SiO(CH_2)_4NCO$ by heating for a short time in DMF in the presence of $PhCO_2Na$,[131] and the preparation of polymeric cyanurate-containing siloxanes by the polycyclotrimerisation of the corresponding dicyanates according to scheme 32,[132,133] have been reported:

Scheme 32



The trimerisation of isocyanates is widely used to produce organic isocyanaurates.[134,135] In the chemistry of the heteroorganic compounds of group IVb, however, practically no use is made of this reaction, since the isocyanates R_3MNCO do not trimerise, and the corresponding data on their carbofunctional analogues are limited to the papers cited above[120–133] for the organosilicon and organotin derivatives.[136,137] In the last papers it is reported that the cyclotrimerisation of $Bu_2RSn.(CH_2)_3N=C=O$ takes place at room temperature to give high yields of the corresponding products (scheme 33):

Scheme 33



R = Bu, Cl .

Data have been published[138,139] on the analogous monosubstituted heterocycle, 2-[γ-(bromodiphenylstannyl)propoxy]-4,6-dichloro-1,3,5-triazine.

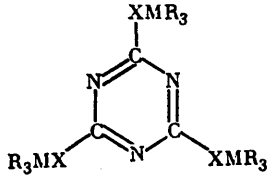
There are no published data on the synthesis and properties of germanium- and lead-containing carbofunctional s-triazines.

III. PHYSICOCHEMICAL PROPERTIES AND STRUCTURE

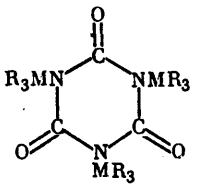
The hetero-organic compounds being considered are glycerol-like colourless or weakly coloured liquids, which boil at high temperatures or cannot be distilled in a vacuum, or vaseline-like or solid products. They are generally soluble in ether, dioxan, benzene, toluene, chloroform, and carbon tetrachloride, and insoluble in water; most hetero-organic s-triazines (except the carbofunctional compounds) are hydrolysed by water. The compounds can be kept practically unchanged for many months in an air-tight vessel. They are extremely stable to heat,[18-21,24] and can be vacuum-distilled with gentle heating. Some of these substances, however, decompose rapidly when heated strongly[12-14,17,49,50] or polymerise.[43,46,76] There are practically no specific published data on these processes, apart from data on the thermal decomposition of tris(trimethylsilyl) cyanurate, which at 280 °C in the pure state[12-14,17] or at 200–230 °C in the presence of chlorine-containing substances[17] decomposes to the monomer, trimethylisocyanatosilane, in quantitative yield. The reaction takes place so cleanly that it can be used to prepare $Me_3SiN{=}C{=}O$. As noted above, an attempt to obtain tris(triethylsilyl) cyanurate from cyanuric chloride and Et_3SiONa (160–200 °C, 1 h) also gave chiefly $Et_3SiN{=}C{=}O$.[17] In contrast to this, heating carbofunctional isocyanates in aprotic solvents gives the opposite result, that is the trimer is formed.[119-131]

Most workers have used IR spectroscopy to prove the structures of the hetero-organic s-triazines obtained. Some information has also been obtained from the NMR,[11,15,29,36,37,84-87,98,115,140] Raman,[15] and mass spectra[15,16,122] of these compounds. Since practically no use has been made of other instrumental methods (ultraviolet spectroscopy, X-ray diffraction), the conclusions reached from the IR and NMR spectra are extremely important. The structure of hetero-organic amino(hydroxy)-derivatives of isocyanuric acid depends chiefly on the nature of the substituent element and also on the volume of the organic groups joined to it. Thus all silicon-substituted non-carbofunctional s-triazines exist in the hydroxy-from (A) (O–Si), and the number of C=N double bonds in the ring corresponds to the number of R_3Si groups.[8-16,26,27,32,33,43,74,76,98-100,107] The explanation is probably that silicon has a higher affinity for oxygen than the other elements of group IVb; this is the reason for the high thermodynamic stability of the Si–O bond.

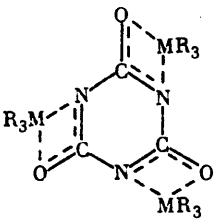
In contrast to this, the organogermanium, -tin, and -lead analogues for all degrees of substitution have the isocyanurate structure (B) (M–N), characterised by the presence of free carbonyl groups, whose IR bands lie in the range 1720–1620 cm^{-1}. Exceptions are the derivatives of ammeline[9,28,33] and ammelide,[99,100] since their R_3M groups (M = Ge, Sn) are joined to the ring through the oxygen atom, as in the organosilicon cyanurates. Tris(benzoyl)ammeline has a similar structure.[17] The fact that these compounds exist only in the form indicated is apparently due to steric hindrance in the formation of the corresponding nitrogen-functional isomers and hence their forced symmetrisation. The structure of the oligodiallyl isocyanurate hetero-organic compounds in Ref.76 can be explained similarly.



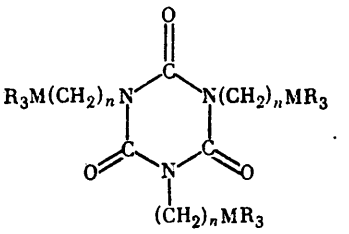
(A) X = O, NH



(B)



(C)



(D)

In addition to the above-mentioned bands due to carbonyl groups, the IR spectra of the organogermanium and organotin isocyanurates also contain bands due to the triazine ring with substituents on the nitrogen atom at 1480–1460 cm^{-1} and 780–760 cm^{-1}.[2,9,17,51] The marked decrease in the C=O stretching wavenumbers in the IR spectra of the organogermanium and organotin s-triazines[9,20,76] is probably due to the decrease in the strength of the C=O bonds as a result of the coordination of adjacent ring nitrogen atoms to the metal atoms, as in organotitanium isocyanurates [form (C)].[141-144] The IR spectra of s-triazines of type (A) contain bands due to the skeletal vibrations of the cyanurate ring at 1580–1515, 1460–1400, and 815–810 cm^{-1}, but do not contain carbonyl group bands.[2,8,9,11,26,28,33,43,74] The hydroxy-structure of the silicon-containing compounds is confirmed by the presence of Si–O–C group bands with a maximum at 1140–1110 cm^{-1}.[8,9,11,15,26]

The hydroxy-form of organosilicon amino(hydroxy)-s-triazines was proved convincingly in an IR and ^1H NMR spectroscopic study of their tri-substituted dimethylsilyl derivatives.[8,11] The ν(Si–H) bands in the IR spectra of these compounds are displaced to higher wavenumbers and increase in the derivative order: melamine–ammeline–ammelide–cyanuric acid. Thus in the first case ν(Si–H) lies at 2140 cm^{-1}, whereas in the last case the wavenumber is increased to 2180 cm^{-1}. This indicates that the Si–H bond in the oxygen-containing organosilicon s-triazines is stronger than that in related compounds containing $H{-}\overset{|}{\underset{|}{Si}}{-}N{=}$ fragments. One reason for this phenomenon is apparently the difference in the degree of conjugation of the Si–O and Si–N bonds. The ν(Si–H) bands of the $Me_2HSiOC{\equiv}$ (E) and $Me_2HSiNH{-}$ (F) groups of tris(dimethylsilyl)ammelide and tris(dimethylsilyl)ammeline were distinguished; they lie at 2170 cm^{-1} and 2160 cm^{-1} for (E) and at 2130 cm^{-1} and 2135 cm^{-1} for (F). The numbers of these fragments can also be estimated from the intensity ratio of the signals of the silyl protons in the ^1H NMR spectra (the chemical shifts for (E) and (F) are 4.92 p.p.m. and 4.60 p.p.m. respectively). Thus the rearrangement of the isocyanurate to the cyanurate system and vice versa may be due either to the introduction of the organosilicon substituents into the isocyanuric acid structure or to the replacement of the latter by other hetero-organic fragments containing group IVb elements[74,75] (section IV, scheme 43). The isomeric transformation of the individual hetero-organic s-triazines is generally irreversible, and in some cases it can be followed by instrumental methods. Thus scheme 14, given in Ref.51, was proved by the IR spectra of the reaction mixtures (50 °C, 5 h), which contain bands due to tris(tributylstannyl) cyanurate [form (A)] at 1560 cm^{-1} and 820 cm^{-1}. When heated to 100–150 °C, the cyanurate is converted into the isocyanurate, as shown by the appearance of bands due to the isocyanurate ring at 1480 cm^{-1} and 780 cm^{-1}, and bands due to the carbonyl groups at 1680–1620 cm^{-1} [form (B)]; the bands characteristic of form (A) disappear. In Refs.23 and 145, the tripropyl- and tributylstannyl derivatives of isocyanuric acid were erroneously assigned to hydroxy-form (A).

As noted above, carbofunctional s-triazines containing group IVb elements usually exist as the isocyanurates, as shown by IR [17,33,58,84,120,122,136,137] and ^{13}C NMR [36,37] spectroscopy. For example, according to Ref.122, $\nu_{as}(C=O)$ for organosilicon s-triazines $[RC_6H_4SiMe_2CH_2NCO]_3$ (R = Hal, p-Me_3C, p-Me_3Si, p-Me_2N) lies at 1680 cm^{-1}, and that for the organotin compounds $[Bu_2Sn(CH_2)_3NCO]_3$ (R = Bu, Cl) at 1700 cm^{-1}, [136,137] that is practically in the range of the carbonyl vibrations of ordinary organic isocyanurates. Bands due to the isocyanurate ring (1470 cm^{-1} and 775 cm^{-1}) were also detected. [136,137]

Data have been published, however, indicating that carbofunctional s-triazines may be formed when tris(allyl) cyanurate is used as the original heterocyclic compound. [4,48,77,78,83] This was confirmed by the IR spectra of the products, which show bands due to the skeletal vibrations of the ring at 820–818 cm^{-1} and the allyloxy-groups at 995–990 cm^{-1} and 950–925 cm^{-1}; the C=O group bands at about 1700 cm^{-1} are not observed. [77]

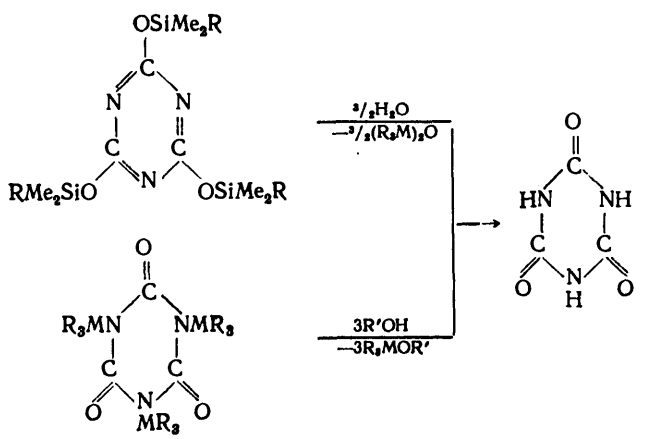
The silicon-containing derivatives of cyameluric acid, like their s-triazine analogues, exist in the O–Si form, and the tin-containing compounds exist in the N-Sn form. [96,97]

Refractometry has also been used in the synthesis and identification of hetero-organic s-triazines, and the study of a series of organosilicon, -germanium, and -tin derivatives of diallyl isocyanurate and isocyanuric acid showed that the average difference between the calculated and experimental values of the molar refraction is −1.20 cm^3 (2σ = 0.15 cm^3). This quantity can be taken as the correction for the isocyanurate ring to the refraction of compounds of this class. [146]

IV. CHEMICAL PROPERTIES

Organosilicon, -germanium, -tin, and -lead s-triazines are extremely reactive substances, but their chemical properties have been insufficiently studied. The best known reactions are those of the hetero-organic derivatives of isocyanuric acid with water and other nucleophilic reagents. Most of these substances are hydrolysed even by atmospheric moisture, so that they can be kept only in air-tight vessels or sealed ampoules. Thus tris(trimethylsilyl) cyanurate and tris(triethylgermyl) isocyanurate are hydrolysed almost instantaneously to isocyanuric acid and hexamethyldisiloxane or hexaethyldigermoxane respectively (scheme 34) [8,11,15,33,52,74] (compare with schemes 2 and 3):

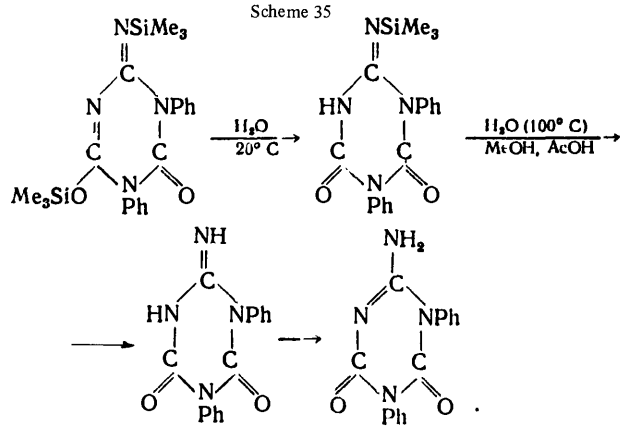
Scheme 34



M = Si, R = H, Me, R′ = H, Me, Bu, $C_{10}H_{21}$, Ph, MeCO, PhCO;
M = Ge, R = Et, R′ = H;
M = Sn, R = Bu, R′ = H, Me, Ph, o-ClC_6H_4, MeCO, PhCO.

The complete hydrolysis of tris(tributylstannyl) isocyanurate requires either a longer time or heating with water. [51] Tris(trimethylsilyl)melamine, -ammeline, and -ammelide, trimethylsilyl diallyl isocyanurate, their triethylgermyl and tributylstannyl analogues, tributylstannyl dicyanoethyl cyanurate, bis(diallyl isocyanurato)dibutylstannane, and other similar compounds are also easily hydrolysed. [9,11,26,28,33,43,105,108,147] The organosilicon imino-s-triazine obtained according to scheme 25 is hydrolysed in stages. [33,105] Its Si–O bond begins to split under the influence of moist air or ether, whereas breakdown of the Si–N bond and separation of the two trimethylsilyl groups require heating with boiling water or treatment with methanol or acetic acid. The final hydrolysis product is apparently an unstable phenyl-substituted isoammelide, which undergoes rearrangement to the corresponding ammelide [33] according to scheme 35:

Scheme 35



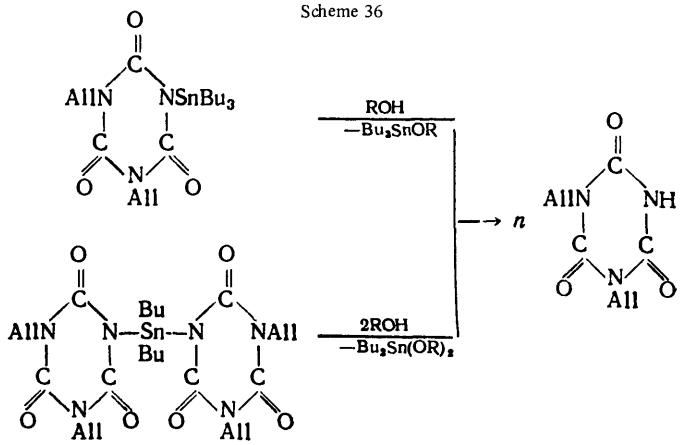
Mild hydrolysis or alcoholysis has also been used to confirm the formation of nitrogen-containing heterocycles in other cycloaddition reactions [98,99,102,108] [schemes 24, 25, and 28).

Unlike the above compounds, silatriazole trimers have an extremely high stability to hydrolysis. For example, diphenylsilyl derivatives of this group are quite stable even when boiled for 2 min with 10% HCl or NaOH. [73]

Carbofunctional s-triazines are also extremely stable to nucleophilic reagents and can even by synthesised in an aqueous-alcoholic or alcoholic medium. [115–118,123–125]

The reactions of tris(trimethylsilyl) cyanurate, [33,74] diallyl tributylstannyl isocyanurate, and bis(diallyl isocyanurato)-dibutylstannane [147] with alcohols, phenols, and carboxylic acids have also been studied (schemes 34 and 36):

Scheme 36

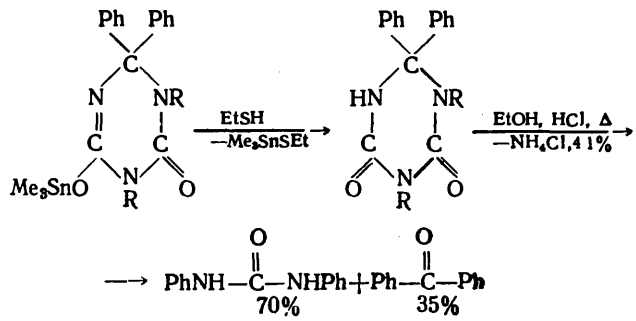


R = Et, Pr, iso-Pr, Ph, MeCO, PhCO, CCl_3CO; n = 1, 2.

The rate and extent of these reactions, and the yields of the final products, depend significantly on the nature of the central atom and the hetero-organic fragments, the reagent used, and the conditions of the process. For example, organosilicon s-triazines are much more reactive than the organotin compounds, and their reaction with hydroxyl-containing compounds is irreversible. This is because isocyanuric acid is chemically inert towards the siloxanes or alkoxy(acyloxy)silanes formed. In contrast to this, the reaction of tris(tributynylstannyl) isocyanurate with methanol is reversible.[25] The replacement of methanol by phenol, acetic acid, or benzoic acid displaced the equilibrium practically completely towards the formation of isocyanuric acid.

The reaction of 1,3,4,4-tetraphenyl-6-trimethylstannyloxy-1,3,5-triazine with ethanethiol in benzene gave the corresponding destannylated s-triazine (scheme 37):[99,100]

Scheme 37



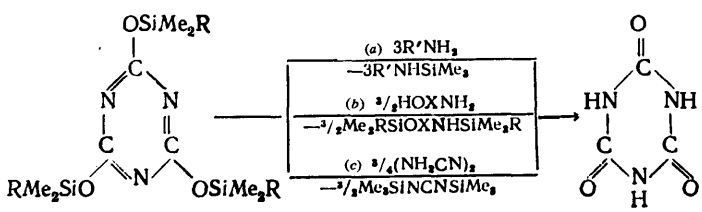
R = Me, Ph .

Subsequent hydrolysis (R = Ph; EtOH + concentrated HCl, 4 d) gave a mixture of benzophenone, N,N'-diphenylurea, and NH_4Cl.[99]

The first stage of scheme 37 has been proposed as a method for synthesising organic triazines with three different substituents on the nitrogen atoms.[99] The yields of the final heterocycles were 76–96%.

Tris(trimethylsilyl) cyanurate reacts on heating with primary amines (100–200 °C, 1–2 h)[33,74] to give isocyanuric acid and mono-substituted silylamines. An interesting feature is that the reaction is reversible. This is particularly noticeable for allylamine, which gives only 50–70% of the corresponding aminosilane (scheme 38). It is for this reason that the latter was used to prepare tris(trimethylsilyl) cyanurate[8,33] (scheme 2).

Scheme 38



R = H, Me; R' = All, Ph, n-C_7H_{15}, cyclohexyl, $Bu_3Sn(CH_2)_3$;

X = CH_2CH_2, $C_6H_4SO_2$.

Since this s-triazine is a fairly powerful silylating agent, the equilibrium for the process (scheme 38a) is determined by the comparative activity of the organosilicon reagents.

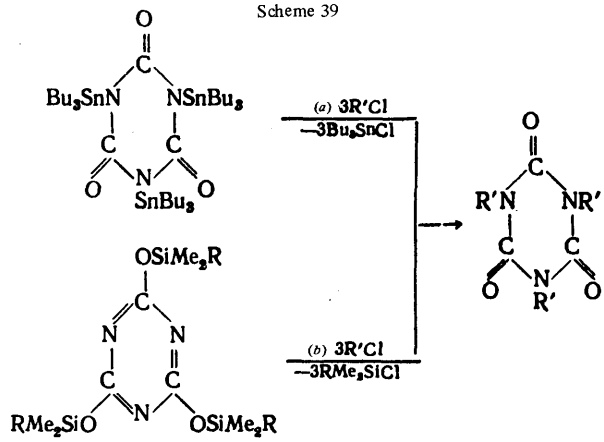
The isocyanuric acid formed when aliphatic amines are used can be removed from the reaction zone as complexes with the original amines (1:1), which decompose to their components above 240 °C.[74]

The reactions of organosilicon cyanurates with bifunctional compounds (2-aminoethanol, sulphanilic acid) do not differ fundamentally from the above reactions and take place according to the general scheme 38b.

The reaction of dicyandiamide with tris(trimethylsilyl) cyanurate gave bis(trimethylsilyl)carbodi-imide in quantitative yield (scheme 38c). The last compound can also be obtained using tris(trimethylsilyl)melamine.[31]

Organosilicon cyanurates do not react with secondary amines, and tris(tributylstannyl) isocyanurate does not react with primary amines either. It reacts readily, however, with carboxylic acid halides, forming tris(acyl) isocyanurates according to scheme 39:[17,25,33,148]

Scheme 39



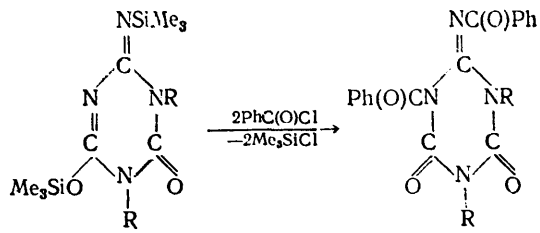
M = Sn, R' = MeCO, PrCO, PhCO, $CH_2CH(CH_3)CO$; M = Si, R = H, Me, R' = MeCO, PhCO, $Me_3Si(CH_2)_3CO$, $(CH_2)_6N{=}C{=}O$, substituted monosaccharides.

Other organotin s-triazines such as tributylstannyl and dibutylstannyl diallyl isocyanurates[147] and tris(tributylstannyl)melamine, -ammeline, and -ammelide[17] are also converted into the corresponding acylated heterocycles by the reaction with acid halides.

Scheme 39a can be used to obtain various acyl derivatives of s-triazines. It gives high yields of the products. High purity of the desired compounds is achieved by replacing the organotin s-triazines by their silicon-containing analogues.

The synthesis of various tris- and bis(acyl) isocyanurates from the corresponding organosilicon s-triazines has been described[10,17,33] (schemes 39b and 40):

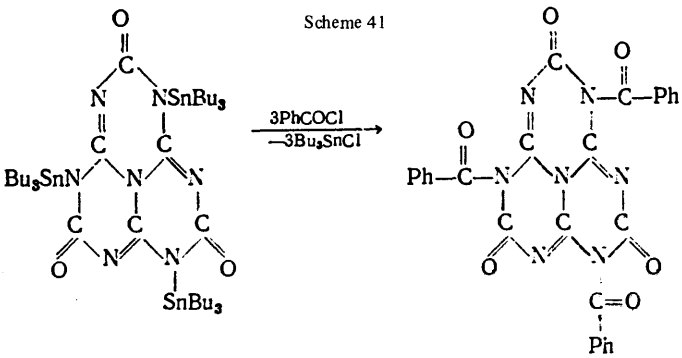
Scheme 40



R = Ph, m-ClC_6H_4 .

Tris(tributylstannyl) cyamelurate also reacts with benzoyl chloride, to give the corresponding tris(benzoyl)derivative[17] in up to 75% yield according to scheme 41:

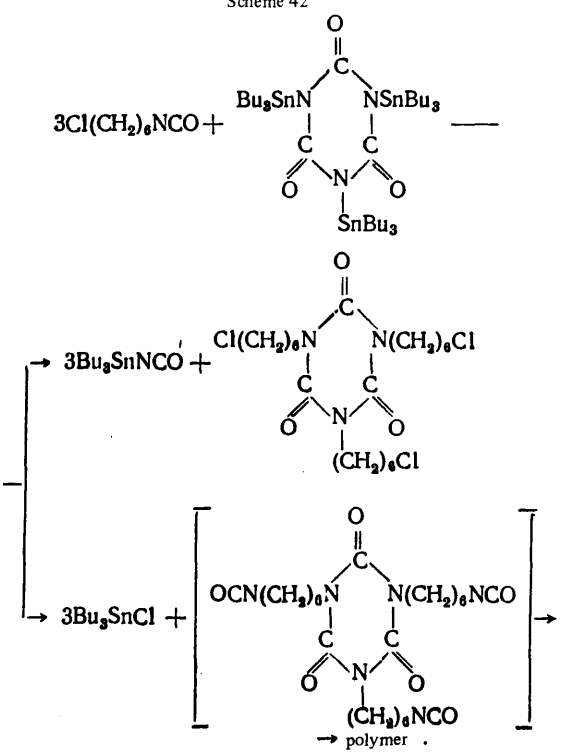
Scheme 41



Hetero-organic s-triazines do not react directly with alkyl halides or aryl halides under normal conditions or on heating,[148] but in some cases reaction takes place in polar aprotic solvents such as DMF. Thus the reaction of tris-(trimethylsilyl) cyanurate with chlorohexamethylene isocyanate gave tris(6-isocyanatohexamethylene) isocyanurate (DMF, 120–170 °C, 3–4 h, yield 96.5%).[149] An interesting feature is that heating a mixture of the same starting materials without a solvent, and heating a mixture of tris-(trimethylsilyl) cyanurate with cyanuric chloride, give exclusively trimethylsilyl isocyanate.[17] Similar splitting of the triazine ring is observed when tris(tributylstannyl) isocyanurate is heated with benzenesulphonyl chloride (120 to 160 °C). At an original reagent ratio of 1:1, tributylstannyl isocyanate is formed in high yield. Change in the ratio to 1:2 or 1:3 leads to the preferential formation of benzenesulphonyl isocyanate. The process is accompanied by considerable tar formation.[25] An attempt to carry out the reaction of tris(trimethylsilyl) cyanurate with ClC(O)NCO (reagent ratio 1:3, ether, 20 °C) gave a polymeric N-substituted tri-isocyanate, which was depolymerised at 150 °C to give 95–97% $(OCN)_2CO$.[150]

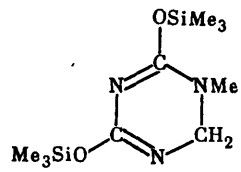
Tris(tributylstannyl) isocyanurate also reacts with $Cl(CH_2)_6NCO$ in DMF with heating to 180–210 °C for 5 h according to scheme 42:[151]

Scheme 42

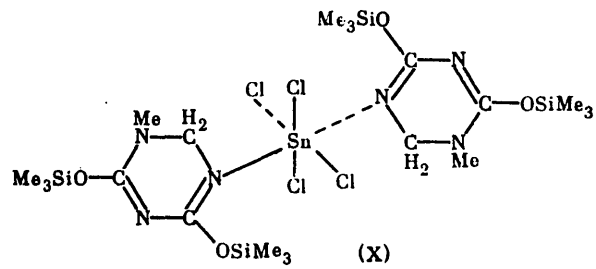


The ability of organosilicon s-triazines to react comparatively easily and quantitatively with active halogen-containing compounds has recently been widely used to synthesise nucleosides. The rate of the reaction is increased in the presence of catalytic quantities of $SnCl_4$,[140,152–158] although the reaction also takes place in its absence.[38,39] Recent investigations of the role of the catalyst[140,153] showed that it forms an intermediate compound (X), which was isolated and characterised from its ^{13}C NMR spectra. Thus the simplified scheme for the preparation of nucleosides [for example (XII)] involves the preliminary synthesis of the organosilicon s-triazine (IX), the intermediate formation of the complex (X), the reaction of the latter with the halogenosaccharide (XI) (the O-acylsaccharide), and the subsequent hydrolysis of the compound formed.[140]

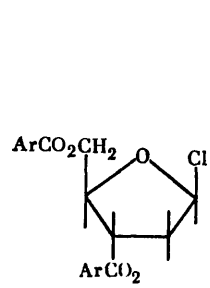
The N-glycosides obtained by these or similar operations can subsequently be methylated or deacetylated when the triazine ring contains N–H groups or the carbohydrate contains Ac–O groups respectively [for example (XIII), (XIV)].



(IX)

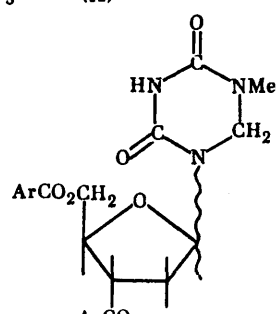


(X)

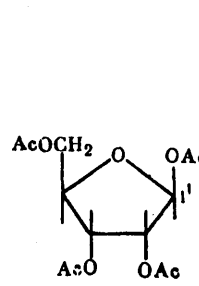


(XI)

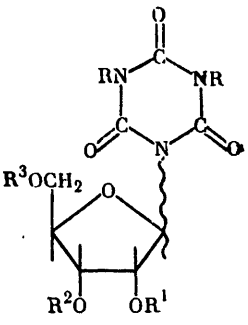
R = H, Me; R^1–R^3 = H, Ac



(XII)



(XIII)

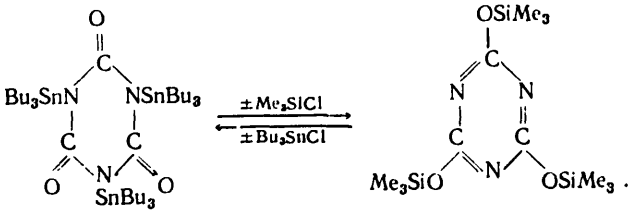


(XIV)

Instead of halogenosaccharides, their acyl derivatives,[152, 159–166] for example tetra-O-acetyl-β-D-ribofuranoside (VIII) [166] are often used. The organosilicon fragments of the s-triazines break the (1′) C–O bond of the O-glycosides and combine with the AcO groups to form compounds of the type Me_3SiOAc and the desired substituted nucleosides (XIV) (N-glycosides). The use of catalysts of the $SnCl_4$ type is necessary. New catalysts for these processes, $Me_3SiOSO_2CF_3$, $Me_3SiOSO_2C_4F_9$, and Me_3SiClO_4, have been proposed.[161] In many cases all the operations described above are carried out in a single stage by heating a mixture of all the starting materials in solvents, but here also the basis is the Gilbert–Johnson method.[161,162] In Refs.163–166, tris(trimethylsilyl) cyanurate prepared by the method of Refs.8 and 10 was used.

As noted above, tris(tributylstannyl) isocyanurate undergoes reversible remetallation with trimethylchlorosilane to give tributylstannyl chloride and a trimethylsilyl derivative of cyanuric acid, which exists in the hydroxy-form, according to scheme 43:[75]

Scheme 43

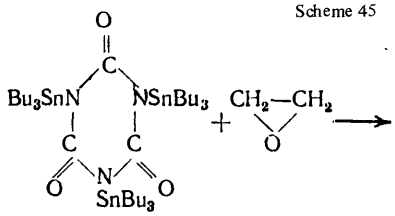


Processes similar to scheme 43 were examined in detail in section II of the present review (schemes 17–21).

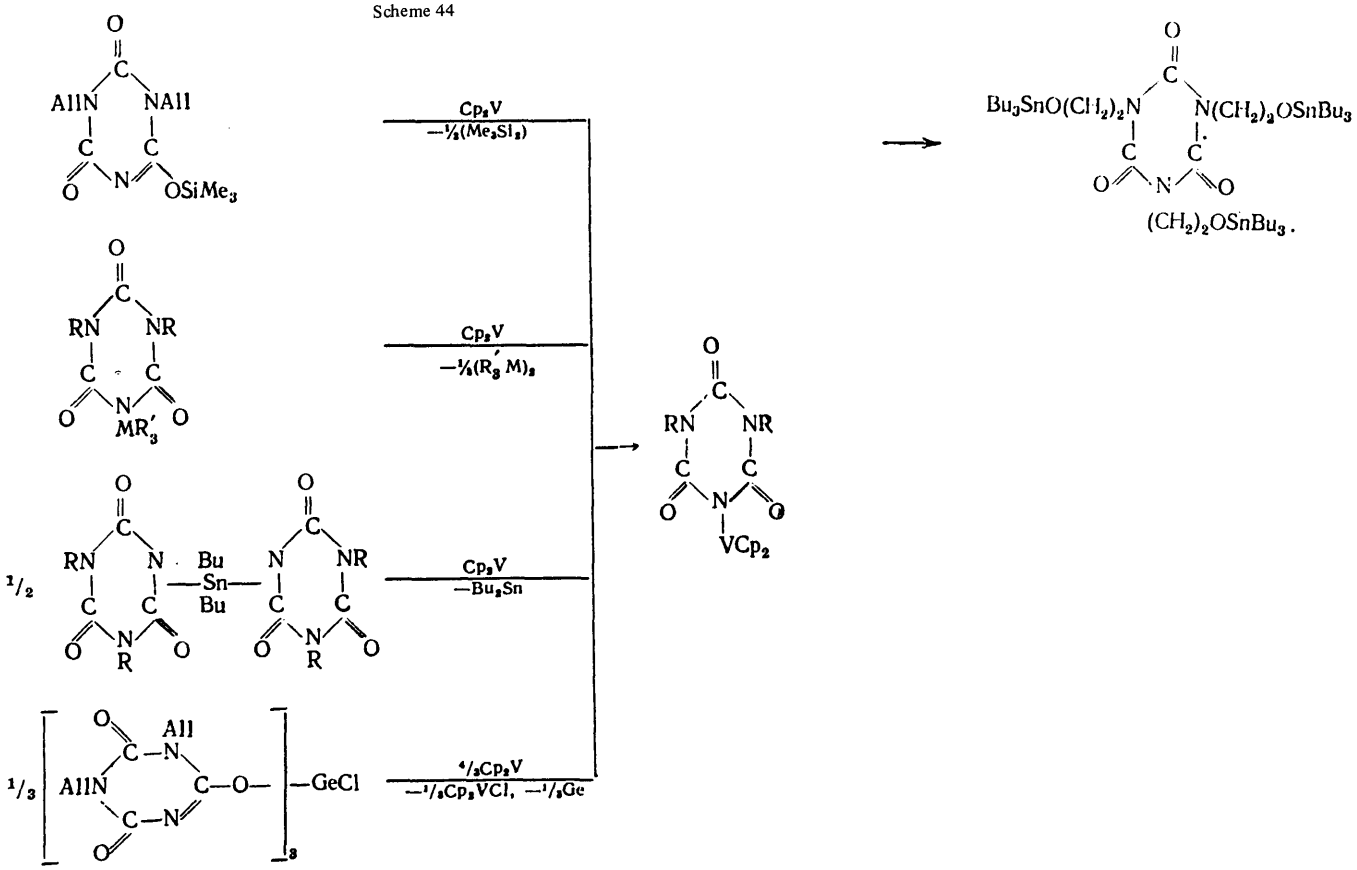
Organosilicon, -germanium, and -tin s-triazines can undergo remetallation not only with hetero-organic compounds of group IVb but also with other compounds. A group of workers including the authors of the present review published a series of papers on the reaction of Si-, Ge-, and Sn-containing derivatives of diallyl and dicyanoethyl isocyanurates with bis-(η^5-cyclopentadienyl)vanadium (Cp_2V) and of trimethylsilyl diallyl isocyanurate with vanadium tetrachloride or tris(acetyl)phosphine.[76] The use of Cp_2V as starting material led to the synthesis of the first representatives of vanadium s-triazines, which are blue–violet crystalline substances, readily oxidised by atmospheric oxygen. The reactions were therefore carried out in toluene in evacuated or argon-filled ampoules [40–50 h, 100–120 °C for the mono- and tris-triazine, and 40 h, 20 °C for the bis-triazine heterocycles (scheme 44)]. The reactivity of the compounds towards Cp_2V increases in the order Si < Ge < Sn.[147,167–170]

The insertion reaction, widely familiar for hetero-organic compounds with an element–nitrogen bond, has been little developed for s-triazines. The only example is the synthesis of tris(β-tributylstannyloxyethyl) isocyanurate using the corresponding organotin s-triazine and ethylene oxide (DMF, heating) according to scheme 45:[5]

Scheme 45



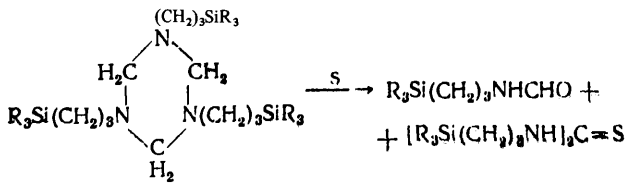
Scheme 44



M = Ge, R′ = Et; M = Sn, R′ = Bu; R = All, $(CH_2)_2Cl \equiv N$ Cp_2V = bis(cyclopentadienyl)vanadium

There are practically no published papers describing the properties of carbofunctional s-triazines. It is known only that 1,3,5-tris-(3-trialkylsilylpropyl)hexahydrotriazine, when heated with sulphur in aqueous alcohol, is converted into a 1:1.6 mixture of N-(3-trialkylsilylpropyl)formamide and N,N'-bis-(3-trialkylsilylpropyl)thiourea (scheme 46):[115-118]

Scheme 46



R = Me, Et, Bu, MeO, EtO.

Data have also been published on the reaction of 2,4-dichloro-6-[(trimethylsilyl)ethynyl]-1,3,5-triazine (scheme 13) with methanol. This reaction does not lead to the rupture of the Si—C bond of the heterocycle, but gives a good yield of the corresponding 2,4-dimethoxy-derivative, which is hydrolysed, but under more severe conditions, to 2-ethynyl-4,6-dimethoxy-1,3,5-triazine.[42]

V. PRACTICAL APPLICATIONS

s-Triazines containing group IVb elements have found extremely varied and extensive practical applications, which are continuing to expand.

The foundation for applied studies in the chemistry of compounds of this class was laid by the synthesis and successful investigation of the possible uses of carbofunctional organosilicon s-triazines and siloxane polymers based on them. They were used to improve the physical or mechanical properties of, or to give specific properties to fibrous materials (wool, viscose, cotton, nylon, glass fibre, etc.) and to prepare heat-resistant, water-resistant, and chemically resistant films and coatings for metals, wood, and various polymers.[54,55,58-66,84-87,123-131,171-182] Thus appropriate treatment of fabrics with triazine polysiloxanes gives them water-repellent properties,[60-65,123-127,182] resistance to repeated washing,[63-65] and wear-resistance.[180,181] These organosilicon products also have increased adhesive properties, so that they are often included in adhesive compositions.[84-87,171-179] The most effective adhesion promoters are isocyanurates of the type $[(RO)_{3-n}R'_nSiR''NCO]_3$, where R, R' = Alk, R'' = CH_2, and also 1,3,5-tris(trimethoxysilylpropyl) isocyanurate. These and other similar compounds are used as vulcanising additives in rubber mixtures, and also as binding and cross-linking agents in the synthesis of various polymers.[78,94,95,132,133,173-181] The synthesis of fluorosiloxanetriazine rubbers and elastomers has been patented.[79-82] These substances and their derivatives have a high thermal stability[59,128-133] and remain practically unchanged on storage.[174]

Organotin s-triazines are used as catalysts and modifying additives in the synthesis of various polymers. For example, tris(triethylstannyl) isocyanurate is used to prepare polyoxymethylene and polyethers with improved colours and transparency.[21,22] The inclusion of tris(tributylstannyl) isocyanurate, -melamine, or cyamelurate in compositions based on polyvinyl chloride gives the polymer increased stability and transparency.[27,183] The stabilising action of organotin s-triazines is increased by their ability to bind the HCl which is liberated when polyvinyl chloride is heated and which increases the rate of the thermal decomposition of this polymer. The binding of HCl by the additives is not decisive, however, since organosilicon cyanurates, which are more reactive towards HCl, are much less effective thermal stabilisers than the tin derivatives.[27] The use of the latter with familiar components (calcium and zinc stearates) gives a synergic effect.

The introduction of tris(tributylstannyl) or tris(trioctylstannyl) isocyanurates into the structures of polymers based on ε-caprolactam gives the resulting polyamide fibre bactericidal properties while preserving its strength and absence of colour.[184]

Tin-containing s-triazines have proved to be extremely effective catalysts for the reactions of isocyanates with alcohols, used in industry for the production of polyurethanes, including their film-forming organosilicon analogues.[6,47,185-193] The tributylstannyl derivatives of these heterocycles, like bis(tributylstannyl) oxide or methoxytributylstannane, have a medium catalytic activity and can be used to obtain polyurethane adhesives and coatings, an important characteristic of which is the stability of the polymer compositions.[193] In contrast to these, dibutylstannyl s-triazines, with an increased catalytic activity, can be recommended for a single-stage method for obtaining polyurethane foam, in which the process should develop vigorously from the moment when the components are mixed.[6,47]

Organotin s-triazines are active and extremely promising bactericides and pesticides with varied spheres of application. Thus they show insecticidal, acaricidal, fungicidal, and algicidal properties and are used to combat bacteria, harmful insects, mites, fungi, parasites in agricultural plants and timber, and also to prevent the fouling of fishing nets, the underwater parts of ships, etc.[19,23,71,72,88-92,138,139,145,194] According to Ref.89, thio-derivatives of tin-containing s-triazines have a low toxicity to warm-blooded animals and can therefore be used to prepare fumigants, detergents, deodorants, coatings for nylon, paper, plastics, wood, etc.

Herbicidal and fungicidal compositions based on organosilicon s-triazines have been patented.[40,195]

Hetero-organic s-triazines are often used as active intermediate compounds for preparing various analogues and derivatives, including bactericidal, pharmaceutical, and medicinal products, polymer additives,[16,34,52,196,197] fabric whiteners,[69] triazinediones,[112] bis(trimethylsilyl)carbodiimide,[49] acylated and germanium-containing analogues difficult to obtain,[9,17,25,28,74,148] and "sandwich" compounds of vanadium.[167-170]

Tris(trimethylsilyl) cyanurate, synthesised comparatively recently, has already been used to obtain trimethylisocyanatosilane,[12-14] carbonyl di-isocyanate $(OCN)_2CO$,[150] bis(trimethylsilyl) carbodi-imide, tris(triethylgermyl) and tris(tributylstannyl) isocyanurates,[74] tris(6-isocyanatohexyl) isocyanurate, which is a strating material for the synthesis of polymers,[149] triacyl isocyanurates,[10,17] and N-glycosides.[163-166]

The last group of compounds, which inlcudes other triazine-containing nucleosides,[38,39,140,152-162,198,199] is of considerable interest for the present authors. These substances are of independent interest as anti-virus, anti-bacteria, and anti-tumour products, and they can also be used in the synthesis of new macrohedral compounds of the nucleotide type.

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While the present review was being prepared for publication, additional papers were published on the synthesis,[200-208] properties,[203,208,209] and practical applications[204-207,210-222] of organosilicon and organotin s-triazines.

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